

**TRIAL BURN PLAN FOR A
TRANSPORTABLE INCINERATION SYSTEM (TIS)
AT THE SAVANNA ARMY DEPOT ACTIVITY (SADA)
WASHOUT LAGOON AREA**

Appendices

Submitted to:

U.S. Army Corps of Engineers
Toxic and Hazardous Waste Management Branch
Kansas City District
Kansas City, Missouri 64106-2896

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UNLIMITED

APPENDIX A

**FEDERAL FACILITY AGREEMENT AMONG U.S. ENVIRONMENTAL
PROTECTION AGENCY (EPA), ILLINOIS ENVIRONMENTAL PROTECTION
AGENCY (IEPA), AND THE U.S. DEPARTMENT OF THE ARMY**

Recovery Act (RCRA), 42 U.S.C. Sections 6961, 6928(h), 6924(u) and (v), as amended by the Hazardous and Solid Waste Amendments of 1984 (HSWA) (hereinafter jointly referred to as RCRA/HSWA or RCRA) and Executive Order 12580;

(ii) U.S. EPA, Region V, enters into those portions of this Agreement that relate to operable unit and final remedial actions pursuant to Section 120(e)(2) of CERCLA/SARA, Sections 6001, 3008(h) and 3004(u) and (v) of RCRA and Executive Order 12580;

(iii) the Army enters into those portions of this Agreement that relate to the RI/FS pursuant to Section 120(e)(1) of CERCLA, Sections 6001, 3008(h) and 3004(u) and (v) of RCRA, the National Environmental Policy Act, 42 U.S.C. Section 4321, the Defense Environmental Restoration Program (DERP), 10 U.S.C. Section 2701 et seq., and Executive Order 12580;

(iv) the Army enters into those portions of this Agreement that relate to operable unit and final remedial actions pursuant to Section 120(e)(2) of CERCLA/SARA, Sections 6001, 3004(u) and (v) and 3008(h) of RCRA, DERP, and Executive Order 12580.

(v) the Illinois Environmental Protection Agency (IEPA) enters into this Agreement pursuant to Sections 120(f) and 121(f) of CERCLA/SARA 42 U.S.C. 9620(f) and 9621(f), Section 3006 of RCRA, 42 U.S.C. Section 6926 and Paragraph 1004 of Chapter 111 1/2 of the Ill. Rev. Stat.

II.

U.S. EPA AND IEPA DETERMINATIONS AND CONCLUSIONS OF LAW

A. While not contesting the authority or jurisdiction of U.S. EPA and IEPA to enter into this Agreement, the Army does not

concur with any of the determinations or conclusions of law contained in this section.

B. On the basis of the results of the testing and analyses described in the Statement of Facts, *infra*, and U.S. EPA and IEPA files and records, the U.S. EPA and IEPA have determined that:

(1) The Savanna Army Depot Activity (SVDA) constitutes a facility within the meaning of 42 U.S.C. Section 9601(9), and Sections 3004(u) and (v), 42 U.S.C. Section 6924(u) and (v), and Section 3008(h), 42 U.S.C. Section 6928(h) of RCRA.

(2) hazardous substances, pollutants or contaminants within the meaning of 42 U.S.C. Sections 9601(14) and (33) and 9604(a)(2) have been disposed of at SVDA;

(3) there have been releases and there continues to be a threat of release of hazardous substances, pollutants or contaminants into the environment within the meaning of 42 U.S.C. Sections 9601(22), 9604, 9606 and 9607 at and from SVDA;

(4) with respect to those releases and threatened releases, the U.S. Army is a responsible person within the meaning of 42 U.S.C. Section 9607;

(5) any corrective actions and any other response measures to be taken pursuant to this Agreement are reasonable and necessary to protect the public health or welfare or the environment; and

(6) SVDA includes a "hazardous waste management facility" as defined under 40 CFR 260.10, authorized to operate

under Sections 3004 and 3005 of RCRA, 42 U.S.C. Sections 6924 and 6925;

(7) The U.S. Army is the owner of the SVDA, as shown on Attachment I.

III.

Findings of Fact

For the purposes of this Agreement, the following constitutes a summary of the facts upon which this Agreement is based. None of the facts related herein shall be considered admissions by any Party. This Section contains findings of facts, determined solely by the U.S. EPA, and shall not be used by any person related or unrelated to this Agreement for purposes other than determining the basis of this Agreement.

1. The Savanna Army Depot Activity (SVDA) occupies 13,062 acres on the east bank of the Mississippi River, 7 miles north of the city of Savanna, in Carroll and Jo Daviess Counties, Illinois.

2. SVDA was activated as the Savanna Proving Ground on 26 December 1918 for the testing of field artillery weapons and ammunition. Ordnance storage facilities were expanded in the 1920s, with the loading and renovation of bombs and artillery shells initiated in the early 1930s. The installation has served a variety of missions since that time; including the burning of several hundred mustard-filled projectiles between 1946 and the

mid-1960s, and the maintenance and storage of radiological materials between 1961 and 1974.

3. SVDA mission activities include handling, processing, testing and storage of munitions and explosives; storage of chemicals; and quality assurance for ammunition, components, missiles, and rockets. SVDA mission support operations include renovation and loading of bombs and artillery shells for transport; demolition and burning of obsolete ordnance; housing of artillery weapons; assembly, disassembly, and storage of munitions; and inspections of equipment.

4. Between 1943 and 1974 ammunition washout operations at SVDA produced wastewater containing various explosives contaminants and was discharged into unlined lagoons. The lagoons overflowed during 1958 and small concentrations of trinitrotoluene (TNT) were found at a sample point where the overflow stream merged with the Crooked Slough Stream, a backwater of the Mississippi River.

5. In September 1978, the U.S. Army Toxic and Hazardous Materials Agency (USATHAMA) initiated the Installation Restoration Program (IRP) and prepared reports entitled Installation Assessment of Savanna Army Depot Activity, Record Evaluation Report No. 134. This report identified 59 potential areas of concern. Potential contaminants included explosive waste and chemical agent (mustard) wastes.

6. In June, 1984, a Hazardous Ranking System (HRS) analysis was performed and identified seven areas of concern.

These areas were: (1) "CL" area TNT melt/pour facility, (2) "CF" area TNT melt/pour facility, (3) Old Sanitary landfill, (4) Active burning grounds, (5) Ammunition demolition area, (6) H-mustard burn, and (7) TNT washout facility leaching ponds. This analysis documents releases of contaminants by four of these areas to surface water bodies.

7. The HRS analysis detected five contaminants of concern: 2,4,6-trinitrotoluene (2,4,6-TNT), 2,4-dinitrotoluene (2,4-DNT), 2,6-dinitrotoluene (2,6-DNT), 1,3,5-trinitrobenzene (1,3,5-TNB) and cyclotrimethylenetrinitramine (RDX).

8. On and subsequent to November 19, 1980, the Army owned or operated the facility (as defined in 40 U.S.C. Section 260.10), defined in paragraph 9 below.

9. The SVDA Site includes an "interim status hazardous waste management facility" pursuant to Section 3005(e) of RCRA, 42 U.S.C. Section 6925(e) and 40 CFR 270.0.

10. The migration and/or threat of migration of 2,4,6-TNT, 2,4-DNT, 2,6-DNT, 1,3,5-TNB, and RDX into the soils, groundwater and surface waters from the facility, as defined in paragraph 9 above, constitute a release of hazardous waste and hazardous constituents to the environment within the meaning of Section 3008(h) of RCRA, 42 U.S.C. Section 6928(h).

11. In June, 1987, a U.S. EPA RCRA Facility Assessment (RFA) was conducted and identified 35 solid waste management units (SMUs). No further action was recommended for 10 of these units. For the remaining 25 units, either corrective action is known to be needed or there is not enough information known to

characterize any releases from the units. This report also recommended that any corrective action be deferred and incorporated as part of the CERCLA response.

12. SVDA is participating in the Department of Defense Installation Restoration Program (IRP), a program established in 1978 to identify and evaluate hazardous waste sites and develop remedial action alternatives to mitigate environmental impacts from these sites. Several studies, including an installation assessment (1979), environmental risk assessment (1981), environmental surveys (1982), an engineering analysis of remedial measures (1984) a groundwater contamination survey (1988), and an environmental monitoring report (1989) have been performed at SVDA. However, these reports have not undergone technical review by U.S. EPA or IEPA at this time. The studies to date have primarily focused on the TNT washout area leaching lagoons but, when the RI/FS is completed, it will encompass the entire site. Funding for the IRP comes from the Department of Defense Environmental Restoration Account.

IV.

Parties

The Parties to this Agreement are the U.S. EPA, the IEPA, and the U.S. Army, SVDA. The terms of this Agreement shall apply to and be binding upon the U.S. EPA, their agents, employees and contractors for the Site; the IEPA, its agents, employees, and contractors for the Site; and the Army, its agents and employees, for the Site and all subsequent owners, operators and lessees of

SVDA. It shall not be a defense of the Army that their contractors violated any of the terms of this Agreement. The Army will notify U.S. EPA and IEPA of the identity and assigned tasks of each of its contractors performing work under this Agreement upon their selection. This Agreement shall be enforceable against all of the foregoing via the Parties to this Agreement. This Part shall not be construed as an agreement to indemnify any person. The Army shall notify its agents, employees, and contractors for the Site, and all subsequent owners, operators and lessees of SVDA of the existence of this Agreement. Each undersigned representative of a Party certifies that he or she is fully authorized to enter into the terms and conditions of this Agreement and to legally bind such Party to this Agreement.

V.

Definitions

Except as noted below or otherwise explicitly stated, the definitions provided in CERCLA and CERCLA/SARA shall control the meaning of the terms used in this Agreement.

In addition:

A. "Authorized representative" may include a Party's contractors acting in any capacity, including an advisory capacity. For the U.S. Army, no contractor shall be considered an authorized representative.

B. "CERCLA" or "CERCLA/SARA" shall mean the Comprehensive Environmental Response, Compensation and Liability

Act, 42 U.S.C. Section 9601 et seq., as amended by the Superfund Amendments and Reauthorization Act of 1986, Pub. L. 99-499.

C. "Days" shall mean calendar days, unless business days are specified. Any Submittal, Written Notice of Position or written statement of dispute that under the terms of this Agreement would be due on a Saturday, Sunday or holiday shall be due on the following business day.

D. "Feasibility Study" or "FS" means that study which fully evaluates and develops remedial action alternatives to prevent or mitigate the migration or the release of hazardous substances, pollutants or contaminants at and from the Site.

E. "Agreement" shall refer to this document and shall include all Attachments to this document. All such Attachments shall be appended to and made an integral and enforceable part of this document.

F. "Operable Units" or "OU" shall mean all discrete response actions implemented prior to a final remedial action which are consistent with the final remedial action and which are taken to prevent or minimize the release of hazardous substances, pollutants or contaminants so that they do not migrate or endanger public health, welfare or the environment.

G. "SVDA" shall mean the Savanna Army Depot Activity as defined in Section VI of this Agreement.

H. ~~"Remedial Investigation"~~ or "RI" means that investigation conducted to fully determine the nature and extent of the release or threat of release of hazardous substances,

pollutants or contaminants and to gather necessary data to support the feasibility study and endangerment assessment.

I. "RCRA" shall mean the Resource Conservation and Recovery Act, 42 U.S.C. Section 6901 et seq., as amended by the Hazardous and Solid Waste Amendments of 1984, Pub. L. 98-616.

J. "Site" shall include SVDA and any other areas contaminated by the migration of a hazardous substance, pollutant or contaminant from SVDA as discussed in Part VI of this Agreement. The term shall have the same meaning as "facility" as defined by Section 101(9) of CERCLA/SARA, 42 U.S.C. Section 9601(9).

K. "Submittal" shall mean every document, report, schedule, deliverable, work plan or other item to be submitted to U.S. EPA and IEPA pursuant to this Agreement.

L. "Deadlines" shall mean schedules as well as that work and those actions which are to be completed and performed in conjunction with such schedules established pursuant to this Agreement. All submittals subject to deadlines shall be postmarked on or before the scheduled deadline.

M. "U.S. Army" or "Army" shall mean the U.S. Army, its employees, agents, successors, assigns and authorized representatives as well as the Department of Defense (DOD), to the extent necessary to effectuate the terms of this Agreement, including, but not limited to, appropriations and Congressional reporting requirements.

N. "U.S. EPA" shall mean the United States Environmental Protection Agency, its employees and authorized representatives.

O. "Written Notice of Position" shall mean a written statement by a Party of its position with respect to any matter which any other Party may dispute pursuant to Part XV of this Agreement.

P. "IEPA" shall mean the Illinois Environmental Protection Agency, its employees and authorized representatives.

Q. "Agencies" shall mean both the U.S. EPA and the IEPA.

VI.

SVDA - Property Description

SVDA encompasses 13,062 acres of land on the east bank of the Mississippi River, approximately 7 miles north of the city of Savanna, Illinois. The southern boundary is the Apple River and SVDA runs northward for approximately 13 miles. SVDA varies in width from one to four miles and lies between the Mississippi River on the west and the Burlington Northern Railroad (BNR) tracks on the east. A small portion of SVDA lies to the east of the BNR tracks just south of the Jo Daviess - Carroll county line. (See Attachment 1 for a map of SVDA).

VII.

Purpose

A. The general purposes of this Agreement are to:

(1) ensure that the environmental impacts associated with past and present activities at the SVDA are thoroughly

investigated and appropriate remedial action taken as necessary to protect the public health, welfare and the environment;

(2) establish a procedural framework and schedule for developing, implementing and monitoring appropriate response actions at the SVDA in accordance with CERCLA/SARA, the NCP, Superfund guidance and policy, RCRA, RCRA guidance and policy; and

(3) facilitate cooperation, exchange of information and participation of the Parties in such actions.

B. Specifically, the purposes of this Agreement are to:

(1) Identify Operable Unit (OU) alternatives which are appropriate at the Site prior to the implementation of final remedial action(s) for the Site. OU alternatives shall be identified and proposed to the Parties as early as possible prior to formal proposal of OUs to U.S. EPA and IEPA pursuant to CERCLA/SARA. This process is designed to promote cooperation among the Parties in identifying OU alternatives prior to selection of final OUs.

(2) Establish requirements for the performance of an RI at the SVDA, to determine the acceptability of previously performed investigative work, ongoing RI activities (washout lagoons) and any additional work necessary to fully characterize the nature and extent of the threat to the public health or welfare or the environment caused by the release and threatened release of hazardous substances, pollutants or contaminants at the SVDA, and to establish requirements for the performance of a

FS at the SVDA to identify, evaluate, and select alternatives for the appropriate remedial action(s) to prevent, mitigate, or abate the release or threatened release of hazardous substances, pollutants or contaminants at the Site in accordance with CERCLA/SARA.

(3) Identify the nature, objective and schedule of response actions to be taken at the Site. Response actions at the Site shall attain that degree of clean-up of hazardous substances, pollutants or contaminants mandated by CERCLA/SARA.

(4) Implement the selected operable unit and final remedial action(s) in accordance with CERCLA, and meet the requirements of Section 120(e)(2) of CERCLA for an Interagency Agreement between the U.S. EPA, IEPA, and the Army.

(5) Assure compliance through this Agreement, with RCRA and other federal and state hazardous waste laws and regulations for matters covered herein.

(6) Coordinate response actions at the site with the mission and support activities at the SVDA.

(7) Expedite the cleanup process (i.e. shortening the time frames specified in this Agreement, whenever possible) to the extent consistent with protection of human health and the environment.

(8) Provide IEPA involvement in the initiation, development, selection and implementation of remedial actions to be undertaken at SVDA, including the review of all applicable data as it becomes available and development of studies, reports,

and action plans; and to identify and integrate State ARARs into the remedial action process.

(9) Provide for operation and maintenance of any remedial action selected and implemented pursuant to this Agreement.

VIII.

Scope of Agreement

Under this Agreement, the U.S. Army agrees it shall:

1. Conduct Operable Units (OUs) as described in Part IX of this Agreement.
2. Conduct a Remedial Investigation (RI) at the Site as described in Part X of this Agreement.
3. Conduct a Feasibility Study (FS) at the Site including all acceptable RI work currently available and any additional work which is contemplated in this Agreement.
4. Develop remedial action alternative(s) for the Site and implement those remedial actions required by this Agreement for the site as described in Part XII to this Agreement.
5. Provide a schedule for the completion of each such remedial action.
6. Provide arrangements for continuing operation and maintenance of the site.

IX.

Operable Units

The Army agrees that it shall develop the operable units (OU) necessary to protect the public health or welfare or the environment and develop OU monitoring plans, and after consultation with U.S. EPA and IEPA, publish its proposed operable unit alternative(s) for public review and comment. Following public comment, the Army shall select and submit its proposed operable unit alternative(s) to U.S. EPA and IEPA. The U.S. EPA Administrator, in consultation with the Army and IEPA, shall have final approval authority over the selected operable unit alternative(s) for the Site. The approval of the operable unit(s) alternative(s) shall be subject to the terms of Sections XIV and XV of this Agreement. Following final approval by U.S. EPA, the Army shall design, propose and submit a workplan for implementation of the selected operable unit, including appropriate timetables and schedules, to U.S. EPA and IEPA. Following EPA and IEPA approval of the workplan, the Army shall implement the operable unit(s) in accordance with the requirements and time schedules set forth in this Agreement. All operable unit actions shall be undertaken in accordance with 40 CFR Part 300.68 and with the requirements of CERCLA/SARA.

All Submittals and elements of work undertaken pursuant to this Part shall be performed in accordance with the requirements and time schedules set forth in this Agreement. The OUs shall meet the purposes set forth in Part VII of this Agreement.

X.

Remedial Investigation

The Army agrees that it shall develop, implement and report upon a RI of the SVDA which may include information collected prior to the effective date of this Agreement and which is in accordance with the requirements and time schedules set forth in this Agreement. The RI shall meet the purposes set forth in Part VII of this Agreement. The Parties specifically agree that all criteria contained in this Agreement (as is defined by the list of deliverables in Part XIV of this Agreement) relate solely to the scope of the RI and do not reflect a predetermination of the Site clean-up level criteria. The parties further agree that final Site clean-up level criteria will only be determined following completion of the Site-wide Endangerment Assessment.

XI.

Feasibility Study

The Army agrees it shall design, propose, undertake and report upon a FS for the Site which is in accordance with the requirements and time schedules set forth in this Agreement. The FS shall meet the purposes set forth in Part VII of this Agreement.

XII.

Remedial Action Selection and Implementation

Following completion of the RI and the FS, the U.S. Army shall, after consultation with U.S. EPA and IEPA, publish its proposed remedial action alternative(s) for public review and

comment. Following public comment, the Army shall submit its proposed remedial action alternative(s) to U.S. EPA and IEPA. The U.S. EPA Administrator, in consultation with the Army and IEPA, shall make final selection of the remedial action(s) for the Site. The selection of the remedial action(s) shall be subject to the terms of Sections XIV and XV of this Agreement. Following final selection by U.S. EPA, the Army shall design, propose and submit a plan for implementation of the selected remedial action, including appropriate timetables and schedules, to U.S. EPA and IEPA for concurrence. Following U.S. EPA and IEPA concurrence, the Army shall implement the remedial action(s) in accordance with the requirements and time schedules set forth in this Agreement. The purpose of the plan for remedial action is to establish procedures for implementation of selected response actions.

XIII.

Statutory Compliance/RCRA-CERCLA Integration

A. The Parties intend to integrate the Army's CERCLA response obligations and RCRA corrective action obligations which relate to the release(s) of hazardous substances, hazardous wastes, pollutants or contaminants covered by this Agreement into this comprehensive Agreement. Therefore, the Parties intend that activities covered by this Agreement will be deemed to achieve compliance with CERCLA, 42 U.S.C. Section 9601 et seq.; to satisfy the corrective action requirements of Sections 3004(u) and (v) of RCRA, 42 U.S.C. Section 6924(u) and (v) for a RCRA

permit, and Section 3008(h), 42 U.S.C. Section 6928(h), for interim status facilities; and to meet or exceed all applicable or relevant and appropriate Federal and State laws and regulations, to the extent required by Section 121 of CERCLA, 42 U.S.C. Section 9621.

B. Based upon the foregoing, the Parties intend that any remedial action selected, implemented and completed under this Agreement shall be deemed by the parties to be protective of human health and the environment such that remediation of releases covered by this Agreement shall obviate the need for further corrective action under RCRA (i.e., no further corrective action shall be required for releases covered by this Agreement). The parties agree that with respect to releases of hazardous waste and hazardous waste constituents covered by this Agreement, RCRA shall be considered an applicable or relevant and appropriate requirement pursuant to Section 121 of CERCLA.

C. The Parties recognize that the requirement to obtain permits for response actions undertaken pursuant to this Agreement shall be as provided for in CERCLA and the NCP. The Parties further recognize that on-going hazardous waste management activities at the SVDA may require the issuance of permits (e.g. RCRA Facility Operating Permits) under Federal and State laws. This Agreement does not affect the requirements, if any, to obtain such permits. However, if a permit is issued to the Army for on-going hazardous waste management activities at the Site, U.S. EPA and/or IEPA, subject to the public notice,

comment and hearing requirements provided for under State and Federal law, shall reference and incorporate any appropriate provisions, including appropriate schedules (and the provision for extension of such schedules), of this Agreement into such permit. The Parties intend that the judicial review of any permit conditions which reference this Agreement shall, to the extent authorized by law, only be reviewed under the provisions of CERCLA.

D. Nothing in this Agreement shall alter the Army's authority with respect to removal actions conducted pursuant to Section 104 of CERCLA, 42 U.S.C. Section 9604.

XIV.

Consultation with U.S. EPA and IEPA

A. Applicability:

The provisions of this Part establish the procedures that shall be used by the Army, U.S. EPA, and IEPA, to provide the Parties with appropriate notice, review, comment, and response to comments regarding RI/FS and RD/RA documents, specified herein as either primary or secondary documents. In accordance with Section 120 of CERCLA and 10 U.S.C. Section 2705, the Army will normally be responsible for issuing primary and secondary documents to U.S. EPA and IEPA. As of the effective date of this Agreement, all draft and final reports for any deliverable document identified herein shall be prepared, distributed and subject to dispute in accordance with paragraphs B through J below. U.S. EPA and IEPA will review all documents

in their possession (as listed in this Section) in order to determine the adequacy of the work performed and whether any additional work is necessary. Review by U.S. EPA and IEPA shall be completed and notification provided to the Army within 60 days following the effective date of this Agreement.

The designation of a document as "draft" or "final" is solely for purposes of consultation with U.S. EPA and IEPA in accordance with this Part. Such designation does not affect the obligation of the parties to issue documents, which may be referred to herein as "final", to the public for review and comment as appropriate and as required by law.

B. General Process for RI/FS and RD/RA Documents:

1. Primary documents include those reports that are major, discrete portions of RI/FS or RD/RA activities. Primary documents are initially issued by the Army in draft form subject to review and comment by U.S. EPA and IEPA. Following receipt of comments on a particular draft primary document, the Army will respond to the comments received and issue a draft final primary document subject to dispute resolution. The draft final primary document will become the final primary document 30 days after the issuance of a draft final document if dispute resolution is not invoked or as modified by decision of the dispute resolution process.

2. Secondary documents include those reports that are discrete portions of the primary documents and are typically input or feeder documents. Secondary documents are issued by the

Army in draft form, subject to review and comment by U.S. EPA and IEPA. Although the Army will respond to comments received, the draft secondary documents may be finalized in the context of the corresponding primary documents. A secondary document may be disputed at the time the corresponding draft final primary document is issued.

C. Primary Reports:

1. The Army shall complete and transmit draft reports for the following primary documents to U.S. EPA and IEPA for review and comment in accordance with the provisions of this Part:

1. Installation Assessment *
2. Environmental Risk Assessment*
3. Rapid Response Environmental Surveys*
4. Engineering Analysis of Alternative Remedial Measures*
5. Groundwater Contamination Survey*
6. Savanna Army Depot Activity Environmental Monitoring*
7. Work Plan/Sampling Plan/Quality Assurance Project Plan/Health and Safety Plan.
8. Endangerment Assessment
9. RI Report
10. FS Report
11. Proposed Plan
12. Final Plan
13. Remedial Design/Remedial Action Workplan

14. Compliance with Substantive Permit Requirements Report
(CERCLA Section 121)

15. Operable Unit Justification Reports

(*) Documents already submitted to the U.S. EPA and IEPA which have not undergone technical review at this time.

2. Only the draft final reports for the primary documents identified above shall be subject to dispute resolution. The Army shall complete and transmit draft primary documents in accordance with the timetable and deadlines established in Part XXXV of this Agreement.

D. Secondary Documents:

1. The Army shall complete and transmit draft reports for the following secondary documents to U.S. EPA and IEPA for review and comment in accordance with the provisions of this Part:

1. Initial Data Quality Objectives
2. Site Characterization Summary
3. Initial Screening of Alternatives/Petition for ARARS
4. Initial Remedial Action Objectives
5. Detailed Analysis of Alternatives
6. Sampling and Data Results

2. Although U.S. EPA and IEPA may comment on the draft reports for the secondary documents listed above, such documents shall not be subject to dispute resolution except as provided by paragraph B hereof. Target dates shall be

established for the completion and transmission of draft secondary reports pursuant to Part XXXV of this Agreement.

E. Meetings of Project Managers on Development of Reports:

The Project Managers shall meet approximately every ninety (90) days, except as otherwise agreed to by the Parties, to review and discuss the progress of work being performed at the site on the primary and secondary documents. Prior to preparing any draft report specified in Paragraphs C and D above, the Project Managers shall meet to discuss the reports results in an effort to reach a common understanding, to the maximum extent practicable, with respect to the results to be presented in the draft report.

F. Identification and Determination of Potential ARARs:

1. For those primary reports or secondary documents that consist of or include ARAR determinations, prior to the issuance of a draft report, the Project Managers shall meet to identify and propose, to the best of their ability, all potential ARARs pertinent to the report being addressed. The IEPA shall identify all potential State ARARs as early in the remedial action process as possible consistent with the requirements of the NCP. SVDA shall consider any written interpretations of ARARs provided by IEPA. Draft ARAR determinations shall be prepared by the Army in accordance with Section 121(d)(2) of CERCLA, the NCP and pertinent guidance issued by U.S. EPA, which is not inconsistent with CERCLA and the NCP.

2. In identifying potential ARARs, the parties recognize that actual ARARs can be identified only on a site-specific basis and that ARARs depend on the specific hazardous substances, pollutants and contaminants at a site, the particular actions proposed as a remedy and the characteristics of a site. The parties recognize that ARAR identification is necessarily an iterative process and that potential ARARs must be re-examined throughout the RI/FS process until a ROD is issued.

G. Review and Comment on Draft Reports:

1. The Army shall complete and transmit each draft primary report to U.S. EPA and IEPA on or before the corresponding deadline established for the issuance of the report. The Army shall complete and transmit the draft secondary document in accordance with the target dates established for the issuance of such reports established pursuant to Part XXXV of this Agreement.

2. Unless the Parties mutually agree to another time period, all draft reports shall be subject to a 30 day period for review and comment. Review of any document by the U.S. EPA and IEPA may concern all aspects of the report (including completeness) and should include, but is not limited to, technical evaluation of any aspect of the document, and consistency with CERCLA, the NCP and any pertinent guidance or policy issued by the U.S. EPA. Comments by the U.S. EPA and IEPA shall be provided with adequate specificity so that the Army may respond to the comment and, if appropriate, make changes to the

draft report. Comments shall refer to any pertinent sources of authority or references upon which the comments are based, and, upon request of the Army, the U.S. EPA or IEPA shall provide a copy of the cited authority or reference. In cases involving complex or unusually lengthy reports, U.S. EPA, or IEPA may extend the 30 day comment period for an additional 20 days by written notice to the Army prior to the end of the 30-day period. On or before the close of the comment period, U.S. EPA and IEPA shall transmit by next day mail their joint comments to the Army.

3. Representatives of the Army shall make themselves readily available to U.S. EPA and IEPA during the comment period for purposes of informally responding to questions and comments on draft reports. Oral comments made during such discussions need not be the subject of a written response by the Army on the close of the comment period.

4. In commenting on a draft report which contains a proposed ARAR determination, U.S. EPA and IEPA shall include a reasoned statement of whether they object to any portion of the proposed ARAR determination. To the extent that either Agency does object, each shall explain the basis for their objection in detail and shall identify any ARARs they believe were not properly addressed in the proposed ARAR determination.

5. Following the close of the comment period for a draft report, the Army shall give full consideration to all written comments on the draft report submitted during the comment period. Within 30 days of the close of the comment period on a

draft secondary report, the Army shall transmit to U.S. EPA and IEPA its written response to comments received within the comment period. Within 30 days of the close of the comment period on a draft primary report, the Army shall transmit to U.S. EPA and IEPA a draft final primary report, which shall include the Army's response to all written comments received within the comment period. While the resulting draft final report shall be the responsibility of the Army, it shall be the product of consensus to the maximum extent possible.

6. The Army may extend the 30 day period for either responding to comments on a draft report or for issuing the draft final primary report for an additional 20 days by providing notice to U.S. EPA and IEPA. In appropriate circumstances, this time period may be further extended in accordance with Part XXXVI hereof.

H. Availability of Dispute Resolution for Draft Final Primary Documents

1. Dispute resolution shall be available to the Parties for draft final primary reports as set forth in Part XV.

2. When dispute resolution is invoked on a draft final primary report, work may be stopped in accordance with the procedures set forth in Part XV regarding dispute resolution.

I. Finalization of Reports:

The draft final primary report shall serve as the final primary report if no party invokes dispute resolution regarding the document or, if invoked, at completion of the dispute

resolution process should the Army's position be sustained. If the Army's determination is not sustained in the dispute resolution process, the Army shall prepare, within not more than 35 days, a revision of the draft final report which conforms to the results of dispute resolution. In appropriate circumstances, the time period for this revision period may be extended in accordance with Part XXXVI hereof.

J. Subsequent Modification of Final Reports:

Following finalization of any primary report pursuant to Paragraph I above, U.S. EPA, IEPA or the Army may seek to modify the report, including seeking additional field work, pilot studies, computer modeling or other supporting technical work, only as provided in Paragraph 1 and 2 below.

1. U.S. EPA, IEPA or the Army may seek to modify a report after finalization if it determines, based on new information (i.e., information that became available, or conditions that became known, after the report was finalized) that the requested modification is necessary. U.S. EPA, IEPA or the Army may seek such a modification by submitting a concise written request to the Project Manager of the other Parties. The request shall specify the nature of the requested modification and how the request is based on new information.

2. In the event that a consensus is not reached by the Project Managers on the need for a modification, either U.S. EPA, IEPA or the Army may invoke dispute resolution to determine if such modification shall be conducted. Modification of a

report shall be required only upon a showing that: (1) the requested modification is based on significant new information, and (2) the requested modification could be of significant assistance in evaluating impacts on the public health or the environment, in evaluating the selection of remedial alternatives, or in protecting human health and the environment.

3. Nothing in this Subpart shall alter U.S. EPA's or IEPA's ability to request the performance of additional work which was not contemplated by this Agreement. The Army's obligation to perform such work must be established by either a modification of a report or document or by amendment to this Agreement.

XV.

Resolution of Disputes

Except as specifically set forth elsewhere in this Agreement, if a dispute arises under this Agreement the procedures of this Part shall apply.

All Parties to this Agreement shall make reasonable efforts to informally resolve all disputes at the Project Manager or immediate supervisor level. If resolution cannot be achieved informally, the procedures of this Part shall be implemented to resolve a dispute.

A. Within thirty (30) days after: (1) the issuance of a draft final primary document pursuant to part XIV of this Agreement, or (2) any action which leads to or generates a dispute, the disputing party shall submit to the Dispute

Resolution Committee (DRC) a written statement of dispute setting forth the nature of the dispute, the work affected by the dispute, the disputing Party's position with respect to the dispute and the technical, legal or factual information the disputing party is relying upon to support its position.

B. Prior to any Party's issuance of a written statement of dispute, the disputing Party shall engage the other Parties in informal dispute resolution among the project managers and/or their immediate supervisors. During this informal dispute resolution period the Parties shall meet as many times as is necessary to discuss and attempt resolution of the dispute.

C. The DRC will serve as a forum for resolution of disputes for which agreement has not been reached through informal dispute resolution. The Parties shall each designate one individual and an alternate to serve on the DRC. The individuals designated to serve on the DRC shall be employed at the policy level (Senior Executive Service (SES) or equivalent) or be delegated the authority to participate on the DRC for the purposes of dispute resolution under this Agreement. The U.S. EPA representative on the DRC is the Waste Management Division Director of U.S. EPA's Region V. The Army's designated member is the Commander, SVDA. The IEPA representative on the DRC is the Deputy Division Manager of the Division of Land Pollution Control. Written notice of any delegation of authority from a Party's designated representative on the DRC shall be provided to all other Parties pursuant to the procedures of Part XVII.

D. Following elevation of a dispute to the DRC, the DRC shall have twenty-one (21) days to unanimously resolve the dispute and issue a written decision signed by all committee members. If the DRC is unable to unanimously resolve the dispute within this twenty-one (21) day period, the written statement of dispute shall be forwarded to the Senior Executive Committee (SEC) for resolution, within seven (7) days after the close of the twenty-one (21) day resolution period.

E. The SEC will serve as the forum for resolution of disputes for which agreement has not been reached by the DRC. The U.S. EPA representative on the SEC is the Regional Administrator of the U.S. EPA's Region V. The Army's representative on the SEC is the Deputy Assistant Secretary of the Army for Environment, Safety and Occupational Health. The IEPA representative on the SEC is the Director of the IEPA. The SEC members shall, as appropriate, confer, meet and exert their best efforts to resolve the dispute and issue a written decision signed by all committee members. If unanimous resolution of the dispute is not reached within twenty-one (21) days, U.S. EPA's Regional Administrator shall issue a written position on the dispute. The Army or IEPA may, within twenty-one (21) days of the Regional Administrator's issuance of U.S. EPA's position, issue a written notice elevating the dispute to the Administrator of U.S. EPA for resolution in accordance with all applicable laws and procedures. Any party electing not to elevate the dispute to the Administrator within the designated twenty-one (21) day

escalation period, shall be deemed to have agreed with the Regional Administrator's written position with respect to the dispute.

F. Upon escalation of a dispute to the Administrator of U.S. EPA pursuant to Subpart E, the Administrator will review and resolve the dispute within twenty-one (21) days. Upon request, and prior to resolving the dispute, the U.S. EPA Administrator shall meet and confer with the Army's Secretariat Representative and/or IEPA to discuss the issue(s) under dispute. Upon resolution, the Administrator shall provide the Army and IEPA with a written final decision setting forth resolution of the dispute. The duties of the Administrator set forth in this Part shall not be delegated.

G. The pendency of any dispute under this Part shall not affect the Army's responsibility for timely performance of the work required by this Agreement, except that the time period for completion of work affected by such dispute shall be extended for a period of time usually not to exceed the actual time taken to resolve any good faith dispute in accordance with the procedures specified herein. All elements of the work required by this Agreement which are not affected by the dispute shall continue and be completed in accordance with the applicable schedule.

H. When dispute resolution is in progress, work affected by the dispute will immediately be discontinued if the Hazardous Waste Division Director for U.S. EPA Region V requests, in writing, that work related to the dispute be stopped because, in

U.S. EPA's and IEPA's opinion, such work is inadequate or defective, and such inadequacy or defect is likely to yield an adverse effect on human health or the environment, or is likely to have a substantial adverse effect on the remedy selection or implementation process. To the extent possible, U.S. EPA and IEPA shall consult with the Army prior to initiating a work stoppage request. After stoppage of work, if the Army believes that the work stoppage is inappropriate or may have potential significant adverse impacts, the Army may meet with the U.S. EPA Division Director and the IEPA Deputy Division Manager to discuss the work stoppage. Following this meeting, and further consideration of the issues, the U.S. EPA Division Director will issue, in writing, a final decision with respect to the work stoppage. The final written decision of the U.S. EPA Division Director may immediately be subject to formal dispute resolution. Such dispute may be brought directly to the SEC, at the discretion of the Army.

I. Within twenty-one (21) days of resolution of a dispute pursuant to the procedures specified in this Part, the Army shall incorporate the resolution and final determination into the appropriate plan, schedule or procedures and proceed to implement this Agreement according to the amended plan, schedule or procedures.

J. Resolution of a dispute pursuant to this Part of the Agreement constitutes a final resolution of such dispute arising under this Agreement. All Parties shall abide by all terms and

conditions of any final resolution of dispute obtained pursuant to this part of this Agreement.

XVI.

Reporting

The Army agrees it shall submit to the U.S. EPA and IEPA monthly written progress reports which describe the actions which the Army has taken during the previous month to implement the requirements of this Agreement. Progress reports shall also describe the activities scheduled to be taken during the upcoming month. Progress reports shall be submitted by the thirtieth (30) day of each month following the effective date of this Agreement. The progress reports shall include a statement of the manner and extent to which the requirements and time schedules set out in the attachments to this Agreement are being met as well as identify any anticipated delays in meeting time schedules, the reason(s) for the delay and actions taken to prevent or mitigate the delay. (See Attachment 2 for monthly reporting format).

XVII.

Notification

A. Unless otherwise specified, any report or Submittal provided pursuant to a schedule or deadline identified in or developed under this Agreement shall be sent by next day mail and addressed or hand delivered to:

U.S. Environmental Protection Agency, Region V
Attn: SVDA Project Manager (IL/IN Unit 1), SHS-11
230 South Dearborn Street
Chicago, Illinois 60604

Illinois Environmental Protection Agency
Attn: SVDA Project Manager
Division of Land Pollution Control
Federal Sites Management Unit
2200 Churchill Road
P.O. Box 19276
Springfield, Il 62794-9276

Documents sent to the Army shall be addressed as follows unless
the Army specifies otherwise by written notice:

--- Commander
Savanna Army Depot Activity
Attn: Environmental Coordinator
SDSLE-VA Building 1
Savanna, Illinois 61074

Commander
U.S. Army Toxic and Hazardous Materials Agency
Attn: SVDA Project Officer
CETHA - IR - R
Building E4435
Aberdeen Proving Ground, MD 21010-5401

All routine correspondences may be sent via regular mail
to the above-named person.

XVIII.

Project Managers and Committees

The U.S. EPA, IEPA, and the Army shall each designate a
Project Manager and Alternate (hereinafter jointly referred
to as Project Manager) for the purpose of overseeing the
implementation of this Agreement. Within ten (10) days of the
effective date of this Agreement, the Parties shall notify each
other of the name and address of its respective Project Manager.
Any Party may change its designated Project Manager by notifying
the other Parties, in writing, within five days of the change.
To the maximum extent possible, communications between the
Parties concerning the terms and conditions of this Agreement

shall be directed through the Project Managers as set forth in Part XVII of this Agreement. Each Project Manager shall be responsible for assuring that all communications from the other Project Managers are appropriately disseminated and processed by the entities which the Project Managers represent.

Subject to the limitations set forth in Part XXI, Subpart A, the U.S. EPA and IEPA Project Managers shall have the authority to: (1) take samples, request split samples of Army samples and ensure that work is performed properly pursuant to the Attachments incorporated into this Agreement; (2) observe all activities performed pursuant to this Agreement, take photographs and make such other reports on the progress of the work as the Project Manager deems appropriate; and (3) review records, files and documents relevant to this Agreement; and (4) direct the Army Project Manager to stop work whenever the U.S. EPA or IEPA Project Manager determines, after discussion with the Army Project Manager, that activity(s) at the site may create a present danger to public health or welfare or the environment. U.S. EPA or IEPA shall, within 24 hours of directing a work stoppage, present the reasons therefor, in writing, to the Army. Within 72 hours of a written request by the Army for review of any directed work stoppage, the U.S. EPA Division Director or the IEPA Deputy Division Manager shall determine, in writing, whether continued work stoppage is necessary to protect public health, welfare, and the environment and possible measures to abate or mitigate the danger. In addition, any Project Manager may

recommend and request field modifications to the work to be performed pursuant to this Agreement, or in techniques, procedures or design utilized in carrying out this Agreement, which are necessary to the completion of the project.

Any field modifications proposed under this Part by any Party must be approved orally by all Project Managers to be effective.

If agreement cannot be reached on the proposed additional work or modification to work, dispute resolution as set forth in Part XV may be used in addition to this Part. Within five (5) business days after oral agreement regarding a modification made pursuant to this Part, the Project Manager who requested the modification shall prepare a memorandum detailing the modification and the reasons therefore and shall provide or mail a copy of the memorandum to the other Project Managers. The Army Project Manager or authorized representative shall be reasonably available to supervise work performed at SVDA during implementation of the work performed pursuant to this Agreement. Each Project Manager shall make him or herself available to the other Project Managers for the pendency of this Agreement. The absence of the U.S. EPA and/or IEPA Project Manager from the Site shall not be cause for work stoppage.

XIX.

Sampling and Data/Document Availability

The Parties shall make available to each other quality assured results of sampling, tests or other data generated by any Party, or on their behalf, with respect to the implementation

of this Agreement within forty-five (45) days of their collection or performance. If quality assurance is not completed within forty-five (45) days, raw data or results shall be submitted within the forty-five (45) day period and quality assured data or results shall be submitted as soon as they become available. If 45 days is inadequate, this deadline can be extended for a period of time necessary for the data to become available, by agreement of all of the Parties.

At the request of the U.S. EPA or IEPA Project Manager, the Army shall allow split or duplicate samples to be taken by the requesting Agency during sample collection conducted during the implementation of this Agreement. The Army's Project Manager shall endeavor to notify the U.S. EPA and IEPA Project Managers not less than ten (10) business days in advance of any sample collection.

XX.

Retention of Records

The federal Parties to this Agreement shall preserve for a minimum of ten (10) years after termination of this Agreement all of its records and documents in its possession or in the possession of its divisions, employees, agents, accountants, contractors or attorneys which relate in any way to the presence of hazardous substances, pollutants and contaminants at the Site or to the implementation of this Agreement, despite any document retention policy to the contrary. After this ten (10) year period, each federal Party shall notify the other parties at

least forty-five (45) days prior to destruction or disposal of any such documents or records. Upon request, the requested Party shall make available such records or documents or copies of any such records or documents or the requesting Party. The IEPA will follow Illinois regulations with respect to retention of records.

XXI.

Access

A. Without limitation on any authority conferred on U.S. EPA or IEPA by statute or regulation, the U.S. EPA, IEPA, and/or their authorized representatives, shall have the authority to enter SVDA at all reasonable times for purposes consistent with this Agreement, subject to statutory and regulatory requirements as may be necessary to protect national security. Such authority shall include, but not be limited to: (1) inspecting records, operating logs, contracts and other documents relevant to implementation of this Agreement; (2) reviewing the progress of the Army, its contractors or lessees in implementing this Agreement; (3) conducting such tests as the U.S. EPA or IEPA Project Manager deem necessary; and (4) verifying the data submitted to the Agencies by the Army. The Army shall honor all reasonable requests for such access by the U.S. EPA and IEPA conditioned only upon presentation of proper credentials. The Army shall provide an escort whenever U.S. EPA and IEPA require access to restricted areas for purposes consistent with the provisions of this Agreement. U.S. EPA and IEPA shall provide reasonable notice to the Army project manager to request any

escorts. U.S. EPA, IEPA and/or their authorized representatives shall not use any camera, sound recording, or other electronic recording devices without permission of the SVDA project manager. However, SVDA shall not unreasonably withhold such permission. When permission must be withheld the Army shall be responsible for alternate arrangements for any work utilizing a camera, sound recording, or other electronic device, if feasible. The Army shall provide, within 48 hours of withholding permission, written explanation of the reasons why alternative arrangements are not feasible.

B. To the extent that access is required to areas of the Site presently owned by or leased to parties other than the Army, the Army agrees to exercise its authorities to obtain access pursuant to Section 104(e) of CERCLA/SARA from the present owners or lessees within thirty (30) calendar days after the need for such access is identified by any of the Parties. Any access agreement obtained by the Army shall provide for reasonable access by U.S. EPA, IEPA and/or their authorized representatives. To the extent that activities pursuant to this Agreement must be carried out on other than Army property, the Army shall notify U.S. EPA and IEPA of such necessity within the 30 day period set forth above. The Army shall use its best efforts to obtain access agreements from the property owners and/or lessors or lessees which shall provide reasonable access to U.S. EPA, IEPA and/or their authorized representatives. The access agreements shall also provide that the owners of any property where

monitoring wells, pumping wells, treatment facilities or other response actions may be located shall notify the Army, IEPA, and the U.S. EPA by certified mail, return receipt requested, at least thirty (30) days prior to any conveyance, of the property owners intent to convey any interest in the property and of the provisions made for the continued operation of the monitoring wells, treatment facilities, or other response actions installed pursuant to this Agreement. In the event that the Army is unable to obtain such access agreements, the Army shall notify U.S. EPA and IEPA, within the 30 day period set forth above, regarding both the lack of agreements and the efforts to obtain such access agreements. U.S. EPA and IEPA may assist the Army, to the extent feasible, in efforts to obtain such access agreements.

XXII.

Five Year Review

Consistent with Section 121(c) of CERCLA/SARA, and in accordance with this Agreement, the Army agrees that U.S. EPA and IEPA will review the remedial action no less often than each five years after the initiation of the final remedial action to assure that human health and the environment are being protected by the remedial action being implemented. If, upon such review, it is the judgment of U.S. EPA, with concurrence of IEPA, that additional action or modification of the remedial action is appropriate in accordance with Section 104 or 106 of CERCLA/SARA, the U.S. EPA shall require the Army to implement such additional

or modified action in accordance with Section XIV.J. of this Agreement.

Any dispute by the Army of the determination by U.S. EPA under this Part shall be resolved under Part XV of this Agreement.

XXIII

Other Claims

Nothing in this Agreement shall constitute or be construed as a bar or release from any claim, cause of action or demand in law or equity by or against any person, firm, partnership or corporation not a signatory to this Agreement for any liability it may have arising out of or relating in any way to the generation, storage, treatment, handling, transportation, release, or disposal of any hazardous substances, hazardous wastes, pollutants, or contaminants found at, taken to, or taken from the SVDA.

Neither the U.S. EPA or IEPA shall be held as a party to any contract entered into by the Army to implement the requirements of this Agreement.

Subject to part XIII (Statutory Compliance), this Agreement shall not restrict U.S. EPA or IEPA from taking any legal or response action for any matter not specifically part of the work covered by this Agreement.

XXIV.

Other Applicable Laws

All actions required to be taken pursuant to this Agreement shall be undertaken in accordance with the requirements of all applicable state and federal laws and regulations to the extent required by CERCLA/SARA.

XXV.

Confidential Information

The Army may assert a confidentiality claim covering all or part of the information requested by this Agreement. Analytical data shall not be claimed as confidential by the Army. Information determined to be confidential by U.S. EPA pursuant to 40 CFR Part 2 shall be afforded the protection specified therein. If no claim of confidentiality accompanies the information when it is submitted to the Agencies, the information may be made available to the public without further notice to the Army.

XXVI.

Amendment of Agreement

This Agreement can be amended or modified solely upon written consent of all Parties. Such amendments or modifications shall have as the effective date that date on which they are signed by all Parties and notice thereof is provided to each signatory pursuant to Section XVII of this Agreement.

XXVII.

Reservation of Rights

In consideration for the Army's compliance with this Agreement, and based on the information known to the Parties on the effective date of this Agreement, the U.S. EPA and IEPA agree that compliance with this Agreement shall stand in lieu of any administrative, legal and equitable remedies against the Army available to them regarding the currently known release or threatened release of hazardous substances including hazardous wastes, pollutants or contaminants at the Site which are the subject of the RI/FS and which will be addressed by the remedial action provided for under this Agreement; except that nothing in this Agreement shall preclude the U.S. EPA or IEPA from exercising any administrative, legal and equitable remedies available to them to require additional response actions by the Army in the event that: (1) conditions previously unknown or undetected by U.S. EPA or IEPA arise or are discovered at the Site; or (2) U.S. EPA or IEPA receives additional information not previously available concerning the premises which they employed in reaching this Agreement, and the implementation of the requirements of this Agreement are no longer protective of public health and the environment.

Notwithstanding this Part, or any Part of this Agreement, the State of Illinois may obtain judicial review of any final decision of the U.S. EPA on selection of an operable unit or

final remedial action, and may invoke its authority under CERCLA/SARA Sections 121(e)(2) and 121(f).

XXVIII.

Enforceability

A. The Parties agree:

(1) upon the effective date of this Agreement, any standard, regulation, condition, requirement or order which has become effective under CERCLA and is incorporated into this Agreement is enforceable by any person pursuant to Section 310 of CERCLA, and any violation of such standard, regulation, condition requirement or order will be subject to civil penalties under Sections 310(c) and 109 of CERCLA;

(2) all timetables and deadlines associated with the RI/FS shall be enforceable by any person pursuant to Section 310 of CERCLA and any violation of such timetables and deadlines will be subject to civil penalties under Sections 310(c) and 109 of CERCLA;

(3) all terms and conditions of this Agreement which relate to operable unit or final remedial actions, including corresponding timetables, deadlines or schedules, and all work associated with the operable unit or final remedial actions, shall be enforceable by any person pursuant to Section 310(c) of CERCLA and any violation of such terms or conditions will be subject to civil penalties under Sections 310(c) and 109 of CERCLA; and

(4) any final resolution of a dispute pursuant to Part XV of this Agreement which establishes a term, condition, timetable, deadline or schedule shall be enforceable by any person pursuant to Section 310(c) of CERCLA, and any violation of such term, condition, timetable, deadline or schedule will be subject to civil penalties under Sections 310(c) and 109 of CERCLA.

B. Nothing in this Agreement shall be construed as authorizing any person to seek judicial review of any action or work where review is barred by any provision of CERCLA, including Section 113(h) of CERCLA.

C. The Parties agree that all Parties shall have the right to enforce the terms of this Agreement.

XXIX.

Stipulated Penalties

A. In the event that the Army fails to submit a primary document (as defined in Section XIV of this Agreement) to U.S. EPA and IEPA, pursuant to the appropriate timetable or deadline in accordance with the requirements of this Agreement, or fails to comply with a term or condition of this Agreement which relates to an operable unit or final remedial action, U.S. EPA may assess or U.S. EPA and IEPA may jointly assess a stipulated penalty against the Army. A stipulated penalty may be assessed in an amount not to exceed \$5,000 for the first week (or part thereof), and \$10,000 for each additional week (or part thereof) for which a failure set forth in this paragraph occurs.

B. Upon determining that the Army has failed in a manner set forth in Paragraph A, U.S. EPA shall so notify the Army in writing. If the failure in question is not already subject to dispute resolution at the time such notice is received, the Army shall have fifteen (15) days after receipt of the notice to invoke dispute resolution on the question of whether the failure did in fact occur. The Army shall not be liable for the stipulated penalty assessed by U.S. EPA or jointly assessed by U.S. EPA and IEPA if the failure is determined, through the dispute resolution process, not to have occurred. No assessment of a stipulated penalty shall be final until the conclusion of dispute resolution procedures related to the assessment of the stipulated penalty.

C. The annual reports required by Section 120(e)(5) of CERCLA shall include with respect to each final assessment of a stipulated penalty against the Army under this Agreement, each of the following:

1. The facility responsible for the failure;
2. A statement of the facts and circumstances giving rise to the failure;
3. A statement of an administrative or other corrective action taken at the relevant facility, or a statement of why such measures were determined to be inappropriate;

4. A statement of any additional action taken by or at the facility to prevent recurrence of the same type of failure; and
5. The total dollar amount of the stipulated penalty assessed for the particular failure.

D. Stipulated penalties assessed pursuant to this Part shall be payable to the Hazardous Substance Response Trust Fund only in the manner and to the extent expressly provided for in Acts authorizing funds for, and appropriations to, the DOD.

E. Payments made pursuant to Subpart D shall be made to the order of the Hazardous Substance Response Trust Fund and forwarded to the U.S. EPA, Superfund Accounting, P.O. Box 371003M, Pittsburgh, Pennsylvania 15251, Attn: Superfund Collection Office. Copies of all payments to the U.S. EPA shall be provided to the U.S. EPA Project Manager.

F. In no event shall this Part give rise to a stipulated penalty in excess of the amount set forth in Section 109 of CERCLA.

G. This part shall not affect the Army's ability to obtain an extension of a timetable, deadline or schedule pursuant to Part XXXVII of this Agreement.

H. Nothing in this Agreement shall be construed to render any officer or employee of the Army personally liable for the payment of any stipulated penalty assessed pursuant to this part.

XXX.

Conveyance of Title

No conveyance of title, easement, or other interest in the Army property on which any containment system, treatment system, monitoring system or other response action(s) is installed or implemented pursuant to this Agreement shall be consummated by the Army without provision for continued maintenance of any such system or other response action(s). No conveyance of title, easement, or other interest in the Army property shall occur without meeting the requirements of Section 120(h) of CERCLA/SARA and/or regulations issued thereunder. At least thirty (30) days prior to any conveyance, the Army shall notify U.S. EPA and IEPA of the provisions made for the continued operation and maintenance of any response action(s) or system installed or implemented pursuant to this Agreement. U.S. EPA and IEPA will review any such proposed conveyance with regard to any effect it may have on the Remedial Investigation and its potential impact on any operable unit or final remedial action. EPA or IEPA review does not imply any authority to restrict property conveyance.

XXXI.

Public Participation

A. The Parties agree that this Agreement and any subsequent proposed remedial action alternative(s) and subsequent plan(s) for remedial action at the Site arising out of this Agreement shall comply with the administrative record and public

participation requirements of CERCLA/SARA, including Section 117 of CERCLA/SARA, the NCP, and U.S. EPA guidance on public participation and administrative records.

B. The Army shall develop and implement a Public Involvement and Response Plan (PIRP) which responds to the need for an interactive relationship with all interested community elements, both on SVDA and off, regarding activities and elements of work undertaken by the Army. The Army agrees to develop and implement the PIRP in a manner consistent with Section 117 of CERCLA/SARA, the NCP, U.S. EPA guidelines set forth in U.S. EPA's Community Relations Handbook, and any modifications thereto.

C. The public participation requirements of this Agreement shall be implemented so as to meet the public participation requirements applicable to RCRA permits under 40 CFR Part 124 and Section 7004 of RCRA.

D. Any Party issuing a formal press release to the media regarding any of the work required by this Agreement shall advise the other Parties of such press release and the contents thereof, at least 2 business days before the issuance of such press release and of any subsequent changes prior to release.

E. The Army agrees it shall establish and maintain an administrative record at and/or near SVDA in accordance with Section 113(k) of CERCLA/SARA. The administrative record shall be established and maintained in accordance with current and future U.S. EPA policy and guidelines. A copy of each document placed in the administrative record will be provided to the

U.S. EPA and the IEPA. The administrative record index developed by the U.S. Army shall be updated and supplied to U.S. EPA and IEPA on at least a quarterly basis.

F. The Army agrees it shall follow the public participation requirements of CERCLA/SARA Section 113(k) and comply with any written guidance and/or regulations issued by U.S. EPA with respect to such Section.

XXXII.

Public Comment

A. Within fifteen (15) days of the date of the signature of the last Party to sign this Agreement, U.S. EPA shall announce the availability of this Agreement to the public for review and comment. U.S. EPA shall accept comments from the public for a period of forty-five (45) days after such announcement. At the end of the comment period, U.S. EPA shall transmit to the other Parties all comments received during the comment period. All Parties shall review these comments and:

(1) Determine that the Agreement should be made effective in its present form, in which case the Army and IEPA shall be so notified in writing by U.S. EPA, and the Agreement shall become effective on the date said notice is received; or

(2) Determine that modification of the Agreement is necessary, in which case the Army and IEPA will be forwarded a revised Agreement by the U.S. EPA, which includes all required changes to the Agreement.

B. In the event of significant revision or public comment, notice procedures of Sections 117 and 211 of CERCLA/SARA shall be followed and a responsiveness summary shall be published by the U.S. EPA.

C. In the event that modification of the Agreement is determined by U.S. EPA or IEPA to be necessary pursuant to Subpart A(2) above, within twenty (20) days of receipt of the revised Agreement, the Army reserves the right to withdraw from the Agreement. If the Army does not provide U.S. EPA or IEPA with written notice of withdrawal from the Agreement within such twenty (20) day period, the Agreement, as modified, shall automatically become effective on the twenty-first (21) day, and U.S. EPA shall issue a notice to the Parties which specifies what the effective date for the IAG will be.

XXXIII.

Termination

The provisions of this Agreement shall be deemed satisfied upon the receipt of written notice from the U.S. EPA, with concurrence of IEPA, that the Army has demonstrated, to the satisfaction of U.S. EPA and IEPA, that all of the terms of this Agreement have been completed. Upon such demonstration by the Army, said written notice shall not be unreasonably withheld or delayed.

XXXIV.

Effective Date

This Agreement is effective upon issuance of a notice to the Parties by U.S. EPA following implementation of Part XXXII of this Agreement. The effective date shall be the date upon which the notice is received by the Parties.

XXXV.

Deadlines

A. The following deadlines have been established, pursuant to the statutory requirements of Section 120(e)(1) of CERCLA/SARA and in conjunction with the State, for the submittal of draft primary documents pursuant to this Agreement:

B. Within twenty-one (21) days of the effective date of this Agreement, the Army shall propose deadlines for completion of the draft primary documents, listed in Section XIV.C.

Within fifteen (15) days of receipt, U.S. EPA and IEPA, shall review and provide joint comments to the Army regarding the proposed deadlines. Within fifteen (15) days following receipt of the comments, the Army shall, as appropriate, make revisions and reissue the proposal. The Parties shall meet as necessary to discuss and finalize the proposed deadlines. If the Parties agree on proposed deadlines, the finalized deadlines shall be incorporated into the appropriate Work Plans. If the Parties fail to agree within thirty (30) days of receipt of Army revisions on the proposed deadlines, the matter shall immediately

be submitted for dispute resolution pursuant to Part XV of this Agreement.

The final deadlines established pursuant to this paragraph shall be published by U.S. EPA, in conjunction with the State.

C. Within twenty-one (21) days of issuance of the Record of Decision, the Army shall propose deadlines for completion of the following draft primary documents:

1. Remedial Design/Remedial Action Work Plan
2. Compliance with Substantive Permit Requirements Report (CERCLA Section 121)

These deadlines shall be proposed, finalized and published utilizing the same procedures set forth in Paragraph B, above.

D. The deadlines set forth in this Part, or to be established as set forth in this Part, may be extended pursuant to Part XXXVI of this Agreement. The parties recognize that one possible basis for extension of the deadlines for completion of the Remedial Investigation and Feasibility Study Reports is the identification of significant new site conditions during the performance of the remedial investigation.

E. Final deadlines set forth in this Part, or to be established as set forth in this Part, shall be attached to this Agreement.

F. Within twenty-one (21) days of the effective date of this Agreement, the Army shall establish target dates for completion of the draft secondary documents, listed in Section XIV.D.

XXXVI.

Extensions

A. Either a timetable and deadline or a schedule shall be extended upon receipt of a timely request for extension and when good cause exists for the requested extension. Any request for extension by the Army shall be submitted in writing to the Agencies and shall specify:

1. The timetable and deadline or the schedule that is sought to be extended;
2. The length of the extension sought;
3. The good cause(s) for the extension; and
4. Any related timetable and deadline or schedule that would be affected if the extension were granted.

B. Good cause exists for an extension when sought in regard to:

1. An event of force majeure;
2. A delay caused by another party's failure to meet any requirement of this Agreement;
3. A delay caused by the good faith invocation of dispute resolution or the initiation of judicial action;
4. A delay caused, or which is likely to be caused, by the grant of an extension in regard to another timetable and deadline or schedule; and
5. Any other event or series of events mutually agreed to by the Parties as constituting good cause.

C. Absent agreement of the Parties with respect to the existence of good cause, the Army may seek and obtain a determination through the dispute resolution process that good cause exists.

D. Within seven days of receipt of a request for an extension of a timetable and deadline or a schedule, U.S. EPA, with the concurrence of IEPA, shall advise the Army in writing of the Agencies' position on the request. Any failure by U.S. EPA to respond within the 7-day period shall be deemed to constitute concurrence in the request for extension. If either Agency does not concur in the requested extension, the U.S. EPA shall include in its statement of nonconcurrence an explanation of the basis for the position.

E. If there is consensus among the Parties that the requested extension is warranted, the Army shall extend the affected timetable and deadline or schedule accordingly. If there is no consensus among the Parties as to whether all or part of the requested extension is warranted, the timetable and deadline or schedule shall not be extended except in accordance with a determination resulting from the dispute resolution process.

F. Within seven days of receipt of a statement of nonconcurrence with the requested extension, the Army may invoke dispute resolution.

G. A timely and good faith request for an extension shall suspend any assessment of stipulated penalties or application for judicial enforcement of the affected timetable and deadline schedule until a decision is reached on whether the requested extension will be approved. If dispute resolution is invoked and the requested extension is denied, stipulated penalties may be

assessed and may accrue from the date of the original timetable, deadline or schedule. Following the grant of an extension, an assessment of stipulated penalties or an application for judicial enforcement may be sought only to compel compliance with the timetable and deadline or schedule as most recently extended.

XXXVII.

Force Majeure

A Force Majeure shall mean any event arising from causes beyond the control of a Party that causes a delay in or prevents the performance of any obligation under this Agreement, including, but not limited to, acts of God; fire; war; insurrection; civil disturbance; explosion; unanticipated breakage or accident to machinery, equipment or lines of pipe despite reasonably diligent maintenance; adverse weather conditions that could not be reasonably anticipated; unusual delay in transportation; restraint by court order or order of public authority; inability to obtain, at reasonable cost and after exercise of reasonable diligence, any necessary authorizations, approvals, permits or licenses due to action or inaction of any governmental agency or authority other than the Army; delays caused by compliance with applicable statutes or regulations governing contracting, procurement or acquisition procedures, despite the exercise of reasonable diligence; and insufficient availability of appropriated funds, if the Army shall have made timely request for such funds as part of the budgetary process as set forth in Part XXXVIII of this

Agreement. A Force Majeure shall also include any strike or other labor dispute, whether or not within the control of the Parties affected thereby. Force Majeure shall not include increased costs or expenses of Response Actions, whether or not anticipated at the time such Response Actions were initiated.

XXXVIII.

Funding

A. It is the expectation of the Parties to this Agreement that all obligations of the Army arising under this Agreement will be fully funded. The Army agrees to seek sufficient funding through the DOD budgetary process to fulfill its obligations under this Agreement.

B. In accordance with Section 120(e)(5)(B) of CERCLA, 42 U.S.C. Section 9620(e)(5)(B), the Army shall include in its annual report to Congress the specific cost estimates and budgetary proposals associated with the implementation of this Agreement.

C. Any requirement for the payment or obligation of funds, including stipulated penalties and cost reimbursement, by the Army established by the terms of this Agreement shall be subject to the availability of appropriated funds, and no provision herein shall be interpreted to require obligation or payment of funds in violation of the Anti-Deficiency Act, 31 U.S.C. Section 1341. In cases where payment or obligation of funds would constitute a violation of the Anti-Deficiency Act, the dates

established requiring the payment or obligation of such funds shall appropriately adjusted.

D. If appropriated funds are not available to fulfill the Army's obligations under this Agreement, U.S. EPA and IEPA reserve the right to initiate an action against any other person, or to take any response action, which would be appropriate absent this Agreement.

Funds authorized and appropriated annually by Congress under the "Environmental Restoration, Defense" appropriation in the Department of Defense Appropriation Act and allocated by the Deputy Assistant Secretary of Defense, Environment ((DASD)(E)) to the Army will be the source of funds for obligations established by this Agreement consistent with Section 211 of CERCLA/SARA, 10 U.S.C. Chapter 160. However, should the Environmental Restoration, Defense appropriation be inadequate in any year to meet the total Army CERCLA implementation requirements, the DOD shall employ and the Army shall follow a standardized DOD prioritization process which allocates that year's appropriations in a manner which maximizes the protection of human health and the environment. A standardized DOD prioritization model shall be developed and utilized with the assistance of U.S. EPA and the states.

XXXIX

Permits

A. The Parties recognize that under Sections 121(d) and 121(e)(1) of CERCLA/SARA, 42 U.S.C. Sections 9621(d) and

9621(e)(1), and the NCP, portions of the response actions called for by this Agreement and conducted entirely on-site are exempted from the procedural requirement to obtain a federal, state, or local permit but must satisfy all the applicable or relevant and appropriate federal and state standards, requirements, criteria, or limitations which would have been included in any such permit.

When the Army proposes a response action to be conducted entirely on-site which in the absence of Section 121(e)(1) of CERCLA/SARA and the NCP would require a federal or state permit, the Army shall include in its submittal to U.S. EPA and IEPA:

- (1) Identification of each permit which would otherwise be required;
- (2) Identification of the standards, requirements, criteria, or limitations which would have had to have been met to obtain each such permit;
- (3) Explanation of how the response action proposed will meet the standards, requirements, criteria or limitations identified in (2) immediately above.

U.S. EPA and IEPA will provide review and comment of this submittal in accordance with Part XIV provisions for primary documents.

B. Subpart A above is not intended to relieve the Army from the requirement(s) of obtaining a permit whenever it proposes a response action involving the shipment or movement off the SVDA of a hazardous substance.

C. The Army shall notify the U.S. EPA and IEPA in writing of any permits required for off-site activities as soon as it becomes aware of the requirements. Upon request, the Army shall

provide the U.S. EPA and IEPA copies of all such permit applications and other documents related to the permit process.

XXXX.

Removals

Notwithstanding any other provision of this Agreement, the Army retains the right, consistent with Executive Order 12580 and 10 U.S.C. Section 2705, to conduct a removal action to abate an imminent and substantial endangerment to human health or the environment from the release or threat of release of hazardous constituents, hazardous substances, pollutants or contaminants at or from SVDA. Such actions may be conducted at any time, either before or after the issuance of a ROD.

The Army shall provide the U.S. EPA and the IEPA with adequate opportunity for timely review and comment after the Army makes any proposal to carry out such removal actions and before the Army initiates any such removal action. This opportunity for review and comment shall not apply if the removal action is in the nature of an emergency action taken because of imminent and substantial endangerment to human health or the environment and it is the determination of the Army that consultation would be impractical. In such case, the Army shall notify the U.S. EPA and the IEPA in writing within 48 hours of taking such action.

XXXXI.

Quality Assurance

The Army shall use quality assurance, quality control, and chain of custody procedures throughout all field investigation,

sample collection and laboratory analysis activities. The Army shall develop an operable unit or element specific Quality Assurance Project Plan (QAPP), as necessary, for review, comment and approval by U.S. EPA. The QAPP shall be prepared in accordance with EPA document QAMS-005/80 and applicable guidance as developed and provided by U.S. EPA.

In order to prove quality assurance and maintain quality control regarding all samples collected pursuant to this Agreement, the Army shall submit all protocols to be used for sampling and analysis to U.S. EPA and IEPA for review, comment and approval. The Army shall also ensure that any laboratory used for analysis is a participant in a quality assurance/quality control program consistent with EPA guidance and that selection of such laboratory shall be subject to U.S. EPA approval.

The Army shall also ensure that appropriate EPA and IEPA personnel or their authorized representatives will be allowed access to any laboratory used by the Army in implementing this Agreement. Such access shall be for the purpose of validating sample analyses, protocols and procedures required by the Remedial Investigation and Quality Assurance Project Plan.

XXXXII.

Reservation of Rights-Recovery of Federal Expenses

The Parties agree to amend this Agreement at a later date in accordance with any subsequent national resolution of the issue of cost reimbursement.

XXXXIII.

State Cost Reimbursement

A. SVDA, pursuant to its authority under 10 U.S.C. 2701(d), agrees to request funding from Congress and to reimburse IEPA for the costs related to the implementation of the Agreement as provided for in this Section.

B. The amount of reimbursable costs payable under this Agreement shall not exceed \$65,000 per year for the first two years following the effective date of the Agreement as defined by Section XXIV above.

C. Prior to the end of the second year, the amount of reimbursable costs for the subsequent years shall be renegotiated in accordance with any then existing agreement on the subject between DOD and the State of Illinois.

D. If no such agreement has been reached between DOD and the State, SVDA and IEPA agree to negotiate in good faith a cap for future reimbursable costs. If SVDA and IEPA are unable to reach agreement after such negotiations, they shall refer any unresolved issues to dispute resolution as set forth in this Section.

E. Nothing in this Agreement constitutes a waiver of any claims by IEPA for costs expended prior to the effective date of this Agreement.

F. Reimbursable costs shall consist only of expenditures required to be made and actually made by IEPA to fulfill its participation under this IAG. Such services shall include:

1. Timely technical review and substantive comment on reports or studies which SVDA prepares in support of its response actions and submits to the State.
2. Identification and explanation of unique State requirements applicable to military installations in performing response actions, especially State applicable or relevant and appropriate requirements (ARARs).
3. Field inspections to ensure cleanup activities are implemented in accordance with agreed upon conditions between the State and the Army.
4. Support and assistance to SVDA in the conduct of public participation activities in accordance with Federal and State requirements for public involvement.
5. Participation in the review and comment functions of SVDA's Technical Review Committee (TRC).
6. Other services specified in this Agreement, or as agreed to by SVDA and IEPA.

G. All reimbursable costs are subject to Section XXXVIII, Funding. Reimbursable costs must be reasonable; they shall not include payment for any activity for which IEPA receives payment or reimbursement from another agency of the United States Government; they shall not include interest; they shall not include payment for anything violative of Federal or State statutes or regulations; and they must be allocable to the services provided in accordance with paragraph F of this Section. Duplicative laboratory work by one State agency of that of another already reimbursed shall not be reimbursable. Travel expenses shall not exceed those expenses customarily allowed by the IEPA for reimbursement of travel expenses.

H. The Army agrees to submit the costs provided under the proceeding paragraph as part of its request for authorizations

and appropriations in accordance with Section XXXVIII. SVDA agrees to advise IEPA of the status of available funds as soon as the appropriations are enacted and final program allocations are made by DOD to the Army. IEPA shall submit either annual or semi-annual invoices at its discretion. The invoices shall be submitted no later than 180 days following the end of the period for which the expenses are claimed. Any costs incurred during a billing period not reflected in the invoice for that billing period will not be reimbursed. The invoice shall contain an itemized description of all expenses claimed. Within 90 days of receipt of an invoice, SVDA shall pay the invoice or notify the IEPA that SVDA questions or disputes the invoice. The project managers shall confer to resolve the question or dispute. Any unresolved dispute shall be subject to dispute resolution as provided for in this Section.

I. IEPA shall maintain adequate accounting records sufficient to identify all expenses related to this Agreement. IEPA agrees to maintain these financial records for a minimum of five (5) years or as otherwise required by Illinois state statutes or regulations. IEPA agrees to provide SVDA or its designated representative reasonable access to all financial records for the purpose of audit during the period of record retention.

J. The Parties recognize that a necessity for effectuating sufficient funding for this Agreement is the provision by IEPA to SVDA of timely and accurate estimates of reimbursable costs.

Within thirty (30) days of the signing of this Agreement, IEPA shall provide SVDA with cost estimates for all anticipated reimbursable expenses to be incurred for the remainder of the current Federal Government fiscal year and the following fiscal year. At least 150 days before the expiration of the second fiscal year, IEPA shall provide SVDA with cost estimates for all anticipated reimbursable expenses to be incurred during the following two fiscal years. IEPA shall expeditiously notify SVDA if it becomes aware that the cost estimates provided under this Section are no longer substantially accurate and provide in their place new cost estimates.

K. Section XV notwithstanding, any dispute between IEPA and SVDA regarding the application of this Section or any matter this Section controls, including but not limited to allowability of expenses and caps of expenses under paragraphs D and F of this Section, shall be resolved in accordance with this Section.

1. The SVDA and IEPA Project Managers shall be the primary points of contact to coordinate resolution of disputes under this Section.
2. If the SVDA and IEPA Project Managers are unable to resolve a dispute, the matter shall be referred to the Commander, SVDA, and the Deputy Division Manager of Land Pollution Control, as soon as practicable but in any event within five (5) working days.
3. Should the Commander and the Deputy Division Manager be unable to resolve the dispute within ten (10) days, the matter shall be elevated to the Deputy for the Environment, Safety, and Occupational Health, Office of the Assistant Secretary of the Army for Installations and Logistics, and the Director of the IEPA.
4. If SVDA and IEPA are unable to resolve the issues in dispute through the dispute resolution process

described in this Section, IEPA may withdraw as a Party to this Agreement by providing written notice of its withdrawal to each of the Parties. Such withdrawal by IEPA shall terminate IEPA's rights and obligations under this Agreement; provided, however, that any approvals or concurrences by IEPA under or pursuant to this Agreement by IEPA prior to its withdrawal shall continue to have full force and effect as if IEPA were still a Party to this Agreement.

5. -It is the intention of SVDA and IEPA that all cost reimbursement disputes shall be resolved strictly in accordance with this Section; however, the use of informal dispute resolution is encouraged. In the event the Director of the IEPA and the Deputy for the Environment, Safety and Occupational Health, are unable to resolve a dispute, IEPA retains all of its legal and equitable remedies to recover its costs.

IN THE MATTER OF:

THE U.S. DEPARTMENT OF
THE ARMY
SAVANNA ARMY DEPOT ACTIVITY
SAVANNA, ILLINOIS

FEDERAL FACILITY AGREEMENT UNDER CERCLA SECTION 120

IT IS SO AGREED:

By:

Deputy Assistant Secretary of
the Army
Environmental, Safety and
Occupational Health
Office of the Assistant
Secretary of the Army
(I and L)

Date

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IN THE MATTER OF:

THE U.S. DEPARTMENT OF
THE ARMY
SAVANNA ARMY DEPOT ACTIVITY
SAVANNA, ILLINOIS

FEDERAL FACILITY AGREEMENT UNDER CERCLA SECTION 120

IT IS SO AGREED:

By:

Commander, SVDA

Date

IN THE MATTER OF:

THE U.S. DEPARTMENT OF DEFENSE
THE ARMY
SAVANNA ARMY DEPOT ACTIVITY
SAVANNA, ILLINOIS

FEDERAL FACILITY AGREEMENT UNDER CERCLA SECTION 120

IT IS SO AGREED:

By:

Bernard P. Killian
Director
Illinois Environmental
Protection Agency

Date

IN THE MATTER OF:

THE U.S. DEPARTMENT OF DEFENSE
THE ARMY
SAVANNA ARMY DEPOT ACTIVITY
SAVANNA, ILLINOIS

FEDERAL FACILITY AGREEMENT UNDER CERCLA SECTION 120

IT IS SO AGREED:

By:

Assistant Administrator
U.S. Environmental Protection
Agency

Date

IN THE MATTER OF:

THE U.S. DEPARTMENT OF DEFENSE
THE ARMY
SAVANNA ARMY DEPOT ACTIVITY
SAVANNA, ILLINOIS

FEDERAL FACILITY AGREEMENT UNDER CERCLA SECTION 120

IT IS SO AGREED:

By: Valdas V. Adamkus
Regional Administrator
U.S. Environmental Protection
Agency

Date

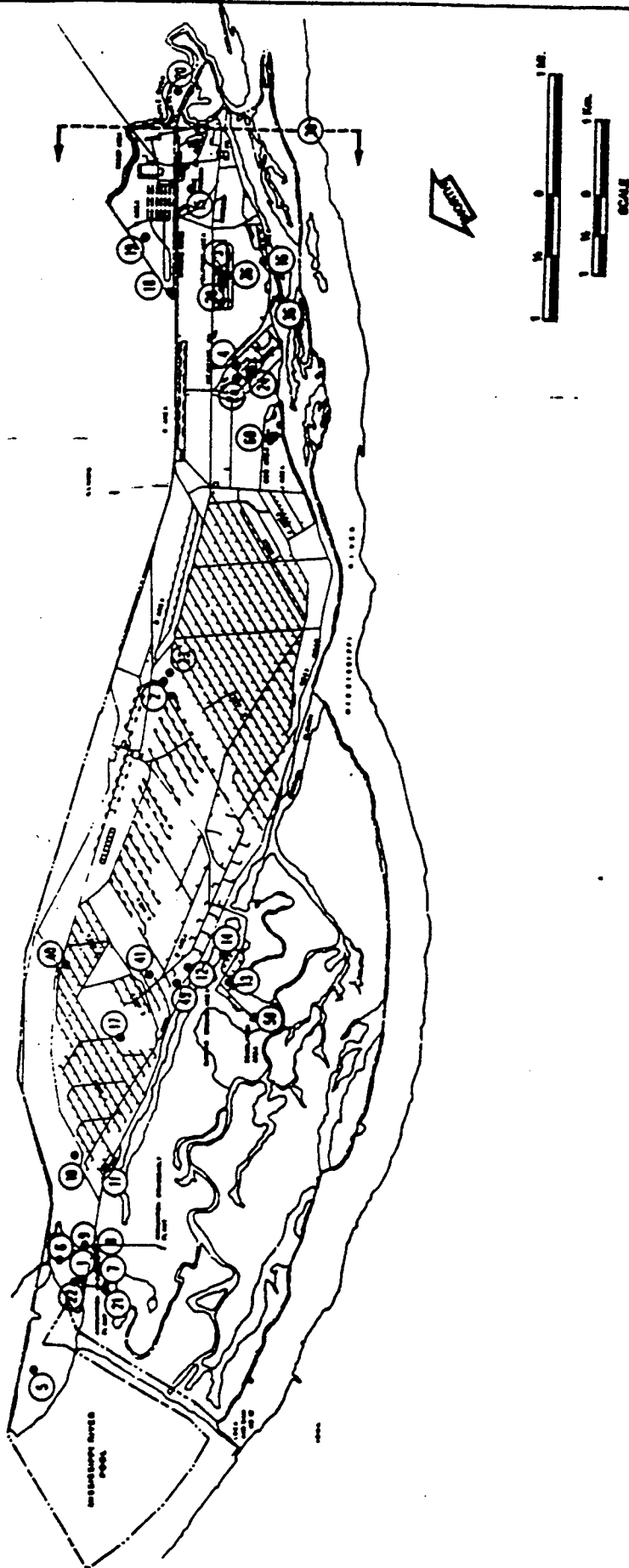
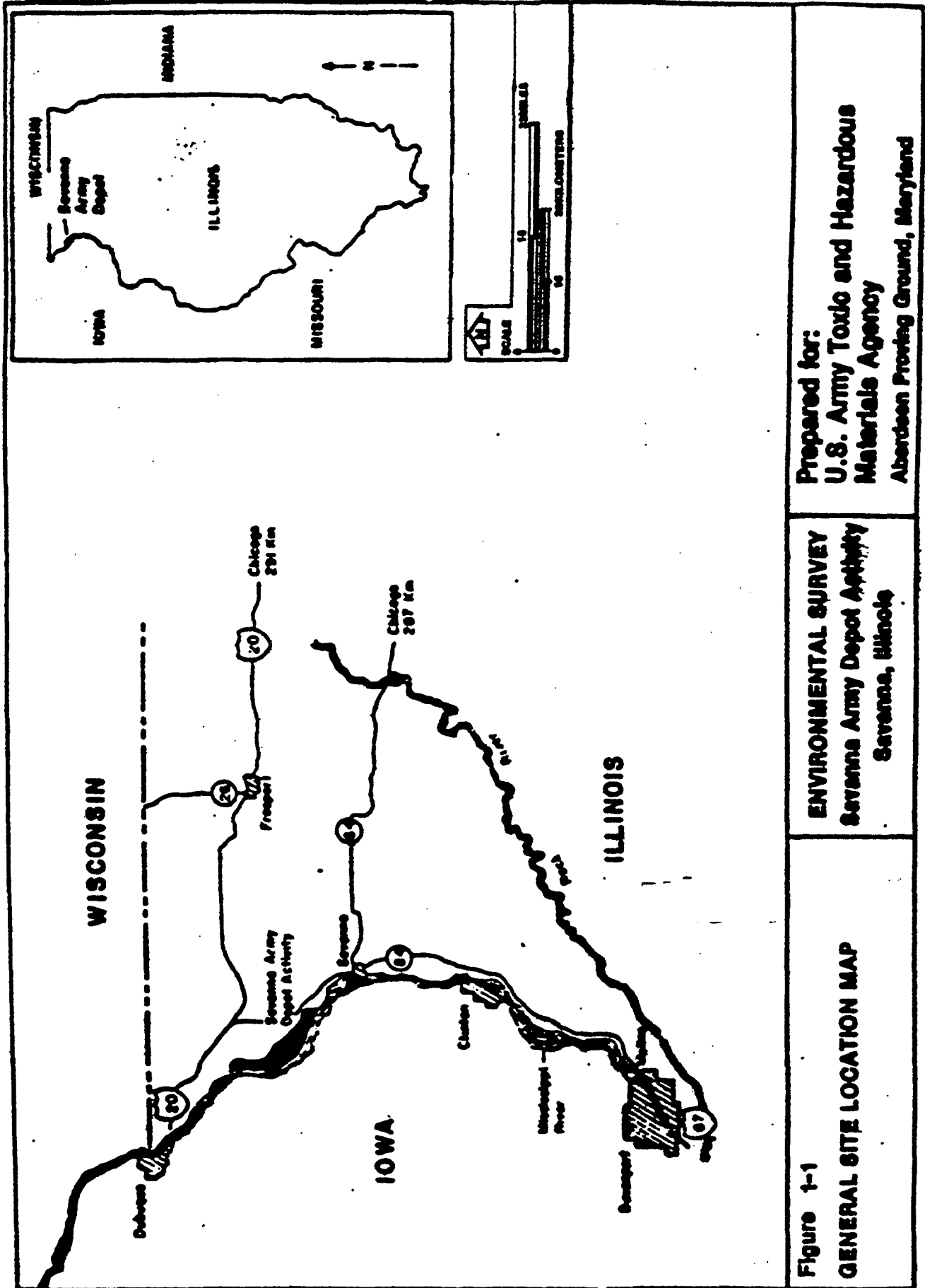


Figure 1-4
MAP OF POTENTIALLY
CONTAMINATED AREAS
 SOURCE: EAE, 1982

Savanna Army Depot Activity

SOURCE: Environmental Sciences and Engineering, Inc., 1980
 Prepared for:
 U.S. Army Toxic and Hazardous
 Materials Agency
 Aberdeen Proving Ground, Maryland



ATTACHMENT II

- Description of the work performed during the past month towards accomplishing the RI objectives.
- Results of all sampling, tests, and all other raw data produced during the past month.
- Scheduled work for the next month.
- A discussion comparing scheduled activity completion including project completion dates versus anticipated activity completion dates and reasons for deviations between these.
- Discussion of problem areas and solutions.
- Name and title of person submitting monthly report and any changes in project personnel.

APPENDIX B

CALCULATIONS FOR THE AMOUNT OF TNT REQUIRED TO DEMONSTRATE A DESTRUCTION AND REMOVAL EFFICIENCY (DRE)



1. TNT stack gas concentration:

$$\text{Conc}_{\text{TNT}} = \frac{\text{TNT}_{\text{DL}} \times 2.2046 \times 10^9}{\text{VM}_{\text{std}}}$$

$$\text{Conc}_{\text{TNT}} = \frac{20 \times 2.2046 \times 10^9}{106}$$

$$\text{Conc}_{\text{TNT}} = 4.16 \times 10^{-10}$$

2. TNT stack gas mass emission rate:

$$\text{MR}_{\text{TNT}} = \text{Conc}_{\text{TNT}} \times \text{VS}_{\text{dscf}} \times 60$$

$$\text{MR}_{\text{TNT}} = 4.16 \times 10^{-10} \times 30,000 \times 60$$

$$\text{MR}_{\text{TNT}} = 7.49 \times 10^{-4}$$

3. Amount of TNT required in feed to measure 99.99 percent DRE:

$$0.9999 = \frac{W_{\text{in}} - \text{MR}_{\text{TNT}}}{W_{\text{in}}}$$

$$W_{\text{in}} = 7.5 \text{ lb/hr}$$

4. Amount of TNT required in feed to measure 99.999 percent DRE:

$$0.99999 = \frac{W_{\text{in}} - \text{MR}_{\text{TNT}}}{W_{\text{in}}}$$

$$W_{\text{in}} = 75 \text{ lb/hr}$$

Reference: "Engineering Analysis of Alternative Remedial Measures, Savanna Army Depot Activity (SADA), Final Report," Prepared for Commander, Savanna Army Depot Activity and Commander, U.S. Army Toxic and Hazardous Materials Agency, Prepared by Roy F. Weston, Inc., November 1984.

APPENDIX C

SUMMARY OF ANALYTICAL DATA FROM REMEDIAL INVESTIGATION REPORT



APPENDIX B

SOIL SAMPLING ANALYTICAL RESULTS

The analytical results presented in Table B-1 were used to evaluate the remedial action alternatives. These data have been input into the IRDMS. When a parameter was analyzed more than once on a particular sample, the average value was used to characterize the soil sample; however, each individual analysis is reported in Table B-1 and not average values.

Detection limits in ug/g for each parameter are listed below. Analytical results lower than these limits are not reported.

<u>HMX</u>	<u>RDX</u>	<u>1,3,5-TNB</u>	<u>1,3-DNB</u>	<u>NB</u>	<u>2A-DNT</u>	<u>2,4,6-TNT</u>	<u>2,6-DNT</u>	<u>2,4-DNT</u>
1.27	0.98	2.09	0.59	0.42	0.29	1.92	0.40	0.42

Detection limits were not constant over the course of the analytical period due to procedural changes (e.g., different volumes of soil were extracted in February/March versus September/October). For example, note that the 2,4,6-TNT detection limit for February/March results was 24 ug/g, whereas the 1.92 ug/g was the detection limit for later analyses.

Although all samples were obtained in January and February 1983 (refer to Table B-2), and all samples were dried, sieved, and extracted at that time, certain samples (mostly with high levels of 2,4,6-TNT) show only a September/October 1983 date of analysis. This is due to certain initial sample analyses being higher than the certified range, and no subsequent dilution and reanalysis was performed at that time. The delay in reanalysis of these samples can be attributed to the sequence of events regarding recertification, delineated in detail in Subsection 3.1.2. Reported September/October results are based on analysis of a newly-prepared extract made from the respective remaining dried, sieved soil samples, and not an analysis of the original (February) extract.

Revision: March 1986

Table B-1

Revision: March 1986

Soil Sampling Analytical Results
Savanna Army Depot

Sample	Explosives concentration in soil, ug/g									Date of Analysis
	HMX	RDX	1,3,5-TNB	1,3-DNB	NB	2A-DNT	2,4,6-TNT	2,6-DNT	2,4-DNT	
<u>Lagoon No. 1</u>										
A007	0 - 0.5 ft		54				71,700			September/October 1983
	0 - 0.5 ft		54				66,400			September/October 1983
A008	0 - 0.5 ft		50				60,100			September/October 1983
	0 - 0.5 ft						54,500			September/October 1983
A017	0 - 0.5 ft	22	55			32	49,000			September/October 1983
A018	0 - 0.5 ft	30	100		20	470	42,000			September/October 1983
	0 - 0.5 ft	44	32			18	46,000			September/October 1983
	0 - 0.5 ft		59			28	38,800			September/October 1983
A019	0 - 0.5 ft					23	15,300			September/October 1983
C013	0 - 0.5 ft		49				9,500			September/October 1983
	0.5 - 1.0 ft		51				31,600			September/October 1983
	1.0 - 1.5 ft						2,780			September/October 1983
	1.5 - 2.0 ft						458			February/March 1983
	2.0 - 2.5 ft						168			February/March 1983
	2.5 - 3.0 ft						32			September/October 1983
	3.0 - 3.5 ft						198			February/March 1983
	3.5 - 4.0 ft						1,224			February/March 1983
	4.0 - 4.5 ft						187			September/October 1983
	4.5 - 5.0 ft						424			February/March 1983
	4.5 - 5.0 ft						424			February/March 1983
C014	0 - 0.5 ft	64	37			106	191,000			September/October 1983
	0.5 - 1.0 ft						1,848			February/March 1983
	1.0 - 1.5 ft		82				1,440			September/October 1983
C015	0 - 0.5 ft	30	96			44	165,000			September/October 1983
	0 - 0.5 ft		93			38	159,000			September/October 1983
	0.5 - 1.0 ft		42			12	143,000			September/October 1983
	1.0 - 1.5 ft	35					14,100			September/October 1983
	1.5 - 2.0 ft						375			February/March 1983
	2.0 - 2.5 ft						112			February/March 1983
	2.5 - 3.0 ft						121			February/March 1983
	3.0 - 3.5 ft						122			February/March 1983

Table B-1
(continued)

Sample	Explosives concentration in soil, ug/g									Date of Analysis
	HMX	RDX	1,3,5-TNB	1,3-DNB	MB	2A-DNT	2,4,6-TNT	2,6-DNT	2,4-DNT	
C016	3.5 - 4.0 ft						106			February/March 1983
	3.5 - 4.0 ft						110			February/March 1983
	4.0 - 4.5 ft						295			February/March 1983
	4.0 - 4.5 ft						280			February/March 1983
	4.5 - 5.0 ft						341			February/March 1983
	4.5 - 5.0 ft						356			February/March 1983
	4.5 - 5.0 ft						386			February/March 1983
	0 - 0.5 ft			50			2,160			September/October 1983
0.5 - 1.0 ft						82			February/March 1983	
1.0 - 1.5 ft						856			February/March 1983	
<u>Lagoon No. 2</u>										
A009	0 - 0.5 ft		27			99	89,600			September/October 1983
	0 - 0.5 ft						89,200			September/October 1983
A012	0 - 0.5 ft	32	117		30	89	135,000			September/October 1983
C017	0 - 0.5 ft						424			September/October 1983
	0 - 0.5 ft						424			February/March 1983
	0.5 - 1.0 ft					13	30			September/October 1983
	1.0 - 1.5 ft						464			February/March 1983
	1.5 - 2.0 ft						24			February/March 1983
	2.0 - 2.5 ft		14				424			February/March 1983
	2.5 - 3.0 ft		12				24			February/March 1983
	3.0 - 3.5 ft						424			February/March 1983
	3.5 - 4.0 ft						424			February/March 1983
	4.0 - 4.5 ft						424			February/March 1983
	4.5 - 5.0 ft						424			February/March 1983
	4.5 - 5.0 ft						424			February/March 1983
C020	0 - 0.5 ft		90			114	200,000			February/March 1983
	0 - 0.5 ft						180,000			September/October 1983
	0 - 0.5 ft		112			143	200,000			September/October 1983
	0.5 - 1.0 ft	43	114			194	192,000			February/March 1983
	0.5 - 1.0 ft						190,000			September/October 1983
	0.5 - 1.0 ft	54	142			243	200,000			September/October 1983
	1.0 - 1.5 ft		50				6,260			September/October 1983
	1.0 - 1.5 ft		102				7,050			September/October 1983
	1.5 - 2.0 ft		37			22	1,264			February/March 1983
	1.5 - 2.0 ft		40				1,440			February/March 1983

Table B-1
(continued)

Sample	Explosives concentration in soil, ug/g									Date of Analysis
	HMX	RDX	1,3,5-TNB	1,3-DNB	NB	2A-DNT	2,4,6-TNT	2,6-DNT	2,4-DNT	
2.0 - 2.5 ft			150			25	960			February/March 1983
2.5 - 3.0 ft			144			15	630			February/March 1983
3.0 - 3.5 ft							222			February/March 1983
3.5 - 4.0 ft							73			September/October 1983
3.5 - 4.0 ft							55			September/October 1983
4.0 - 4.5 ft							54			February/March 1983
4.5 - 5.0 ft							800			February/March 1983
<u>Lagoon No. 3</u>										
A010 0 - 0.5 ft							14,600			February/March 1983
0 - 0.5 ft							13,000			September/October 1983
A013 0 - 0.5 ft							11,300			February/March 1983
0 - 0.5 ft							10,000			September/October 1983
C018 0 - 0.5 ft						182	1,968			February/March 1983
0 - 0.5 ft						176	1,984			February/March 1983
0.5 - 1.0 ft							45,440			February/March 1983
0.5 - 1.0 ft							40,000			September/October 1983
1.0 - 1.5 ft							4,464			February/March 1983
1.5 - 2.0 ft							2,144			February/March 1983
2.0 - 2.5 ft							58,400			February/March 1983
2.0 - 2.5 ft							53,840			February/March 1983
2.0 - 2.5 ft							46,000			September/October 1983
2.5 - 3.0 ft							770			February/March 1983
3.0 - 3.5 ft							440			February/March 1983
3.5 - 4.0 ft							365			February/March 1983
4.0 - 4.5 ft							126			February/March 1983
4.5 - 5.0 ft							126			February/March 1983

Table B-1
(continued)

Sample	Explosives concentration in soil, ug/g								Date of Analysis
	EMX	RDX	1,3,5-TNB	1,3-DNB	NB	2A-DNT	2,4,6-TNT	2,6-DNT	
C021									
0 - 0.5 ft							150,000		February/March 1983
0 - 0.5 ft		28	124				160,000		February/March 1983
0 - 0.5 ft							200,000		September/October 1983
0 - 0.5 ft							192,000		September/October 1983
0.5 - 1.0 ft			61			77	44,800		February/March 1983
0.5 - 1.0 ft			76			91	40,000		September/October 1983
1.0 - 1.5 ft			111				1,192		February/March 1983
1.0 - 1.5 ft			111				1,200		February/March 1983
1.5 - 2.0 ft			14				824		February/March 1983
1.5 - 2.0 ft			84				864		February/March 1983
1.5 - 2.0 ft			80				960		February/March 1983
2.0 - 2.5 ft			61				742		February/March 1983
2.0 - 2.5 ft			61				726		February/March 1983
2.5 - 3.0 ft			37				704		February/March 1983
2.5 - 3.0 ft			45				744		February/March 1983
3.0 - 3.5 ft			52				543		February/March 1983
3.0 - 3.5 ft							553		February/March 1983
3.5 - 4.0 ft			37				595		February/March 1983
3.5 - 4.0 ft			38				554		February/March 1983
4.0 - 4.5 ft							82		February/March 1983
4.0 - 4.5 ft							95		September/October 1983
4.0 - 4.5 ft							128		September/October 1983
4.0 - 4.5 ft							135		September/October 1983
4.5 - 5.0 ft							59		February/March 1983
4.5 - 5.0 ft							51		February/March 1983
Lagoon No. 4									
A011							26,900		September/October 1983
A014			55			305	54,300		September/October 1983
C019						14	400		February/March 1983
0.5 - 1.0 ft							162		February/March 1983
1.0 - 1.5 ft							166		February/March 1983
1.5 - 2.0 ft						22	580		February/March 1983
2.0 - 2.5 ft							70		February/March 1983
2.5 - 3.0 ft							98		February/March 1983
2.5 - 3.0 ft							109		February/March 1983

Table B-1
(continued)

Sample	Explosives concentration in soil, ug/g									Date of Analysis
	EMX	RDX	1,3,5-TNB	1,3-DNB	NB	2A-DNT	2,4,6-TNT	2,6-DNT	2,4-DNT	
	3.0 - 3.5 ft						71			February/March 1983
	3.5 - 4.0 ft						62			February/March 1983
	4.0 - 4.5 ft						40			February/March 1983
	4.5 - 5.0 ft						24			February/March 1983
022	0 - 0.5 ft	23	120			373	85,400			September/October 1983
	0 - 0.5 ft		88				67,000			September/October 1983
	0.5 - 1.0 ft		36			64	4,700			September/October 1983
	0.5 - 1.0 ft						5,960			September/October 1983
	1.0 - 1.5 ft					65	28,400			September/October 1983
	1.5 - 2.0 ft					13	248			February/March 1983
	2.0 - 2.5 ft						215			February/March 1983
	2.5 - 3.0 ft		22			25	334			February/March 1983
	3.0 - 3.5 ft		36				404			February/March 1983
	3.5 - 4.0 ft		22			26	474			February/March 1983
	4.0 - 4.5 ft		22				311			February/March 1983
	4.0 - 4.5 ft		19				330			February/March 1983
	4.0 - 4.5 ft		27				337			February/March 1983
	4.0 - 4.5 ft		19				330			February/March 1983
	4.5 - 5.0 ft						137			February/March 1983
agoon No. 5										
001	0 - 0.5 ft						19,500			September/October 1983
	0 - 0.5 ft						25,600			September/October 1983
003	0 - 0.5 ft		22				507			September/October 1983
	0 - 0.5 ft		19				327			September/October 1983
005	0 - 0.5 ft						175			February/March 1983
015	0 - 0.5 ft						952			February/March 1983
001	0 - 0.5 ft						582			February/March 1983
	0.5 - 1.0 ft						130			February/March 1983
	1.0 - 1.5 ft						43			February/March 1983

Table B-1
(continued)

Sample	Explosives concentration in soil, ug/g								Date of Analysis
	HMX	RDY	1,3,5-TNB	1,3-DNB	KB	2A-DNT	2,4,6-TNT	2,6-DNT	2,4-DNT
C003									
	0 - 0.5 ft						3,392		February/March 1983
	0 - 0.5 ft						6,800		September/October 1983
	0 - 0.5 ft						3,110		September/October 1983
	0.5 - 1.0 ft						119		February/March 1983
	1.0 - 1.5 ft						179		February/March 1983
	1.5 - 2.0 ft						90		February/March 1983
	2.0 - 2.5 ft						398		February/March 1983
	2.5 - 3.0 ft						< 24		February/March 1983
	3.0 - 3.5 ft						< 24		February/March 1983
	3.5 - 4.0 ft						< 24		February/March 1983
	4.0 - 4.5 ft						< 24		February/March 1983
	4.5 - 5.0 ft						< 24		February/March 1983
C005									
	0 - 0.5 ft						1,072		February/March 1983
	0 - 0.5 ft						1,000		September/October 1983
	0.5 - 1.0 ft						232		February/March 1983
	1.0 - 1.5 ft						43		February/March 1983
C007									
	0 - 0.5 ft						49		February/March 1983
	0.5 - 1.0 ft						44		February/March 1983
	1.0 - 1.5 ft						< 24		February/March 1983
	1.5 - 2.0 ft						35		February/March 1983
	1.5 - 2.0 ft						35		September/October 1983
	2.0 - 2.5 ft						24		February/March 1983
	2.5 - 3.0 ft						< 24		February/March 1983
	2.5 - 3.0 ft						< 24		September/October 1983
	3.0 - 3.5 ft						< 24		February/March 1983
	3.5 - 4.0 ft						< 24		February/March 1983
	4.0 - 4.5 ft						< 24		February/March 1983
	4.0 - 4.5 ft						< 24		September/October 1983
	4.5 - 5.0 ft						< 24		February/March 1983
	4.5 - 5.0 ft						< 24		September/October 1983
C011									
	0 - 0.5 ft						521		February/March 1983
	0.5 - 1.0 ft						152		February/March 1983
	1.0 - 1.5 ft						29		February/March 1983
	1.5 - 2.0 ft						43		February/March 1983
	2.0 - 2.5 ft						284		February/March 1983
	2.5 - 3.0 ft						35		February/March 1983
	3.0 - 3.5 ft						< 24		February/March 1983
	3.5 - 4.0 ft						< 24		February/March 1983
	4.0 - 4.5 ft						< 24		February/March 1983
	4.5 - 5.0 ft						< 24		February/March 1983

Table B-1
(continued)

Sample	Explosives concentration in soil, ug/g								Date of Analysis
	HMX	RDX	1,3,5-TNB	1,3-DNB	NB	2A-DNT	2,4,6-TNT	2,6-DNT	
Lagoon No. 6									
A002	0 - 0.5 ft		42				3,480		September/October 1983
A004	0 - 0.5 ft						1,600		February/March 1983
A006	0 - 0.5 ft						82		February/March 1983
A016	0 - 0.5 ft	35	58				60,000		September/October 1983
	0 - 0.5 ft		96				66,900		September/October 1983
C002	0 - 0.5 ft						150		February/March 1983
	0.5 - 1.0 ft						121		February/March 1983
	1.0 - 1.5 ft						82		February/March 1983
C004	0 - 0.5 ft	18	57				66,200		September/October 1983
	0.5 - 1.0 ft						258		February/March 1983
	1.0 - 1.5 ft						279		February/March 1983
	1.0 - 1.5 ft						284		February/March 1983
	1.5 - 2.0 ft						424		February/March 1983
	2.0 - 2.5 ft						352		February/March 1983
	2.5 - 3.0 ft						424		February/March 1983
	3.0 - 3.5 ft						424		February/March 1983
	3.5 - 4.0 ft						424		February/March 1983
	3.5 - 4.0 ft						26		February/March 1983
	4.0 - 4.5 ft						424		February/March 1983
	4.5 - 5.0 ft						424		February/March 1983
C006	0 - 0.5 ft		30				5,290		September/October 1983
	0.5 - 1.0 ft						215		February/March 1983
	1.0 - 1.5 ft						375		February/March 1983
	1.5 - 2.0 ft						43		February/March 1983
	2.0 - 2.5 ft						137		February/March 1983
	2.5 - 3.0 ft						424		February/March 1983
	3.0 - 3.5 ft						424		February/March 1983
	3.5 - 4.0 ft						424		February/March 1983
	4.0 - 4.5 ft						38		February/March 1983
	4.5 - 5.0 ft						424		February/March 1983

Table B-1
(continued)

Sample	Explosives concentration in soil, ug/g									Date of Analysis
	HMX	RDX	1,3,5-TNB	1,3-DNB	NB	2A-DNT	2,4,6-TNT	2,6-DNT	2,4-DNT	
C008										
0 - 0.5 ft							1,440			February/March 1983
0 - 0.5 ft							1,500			September/October 1983
0.5 - 1.0 ft							146			February/March 1983
1.0 - 1.5 ft							75			February/March 1983
1.5 - 2.0 ft							424			February/March 1983
1.5 - 2.0 ft							424			September/October 1983
2.0 - 2.5 ft							180			February/March 1983
2.5 - 3.0 ft							24			February/March 1983
3.0 - 3.5 ft							424			February/March 1983
3.5 - 4.0 ft							424			February/March 1983
4.0 - 4.5 ft							424			February/March 1983
4.5 - 5.0 ft							424			February/March 1983
C012										
0 - 0.5 ft							1,430			September/October 1983
0.5 - 1.0 ft							386			February/March 1983
1.0 - 1.5 ft							87			February/March 1983
<u>Overflow Trench</u>										
T001										
0 - 0.5 ft			71				65,900			September/October 1983
0 - 0.5 ft							67,200			September/October 1983
0.5 - 1.0 ft			39				6,330			September/October 1983
1.0 - 1.5 ft	NA	NA		NA	NA	NA	1,100	NA	NA	September/October 1983
1.5 - 2.0 ft							1,280			February/March 1983
T002						13				
0 - 0.5 ft			78				57,300			September/October 1983
0 - 0.5 ft			67				48,000			September/October 1983
0 - 0.5 ft			66				50,600			September/October 1983
0.5 - 1.0 ft			99				24,730			September/October 1983
0.5 - 1.0 ft							23,850			September/October 1983
1.0 - 1.5 ft							469			September/October 1983
1.0 - 1.5 ft							538			February/March 1983
1.5 - 2.0 ft			46		20		3,720			September/October 1983
1.5 - 2.0 ft			28				3,820			September/October 1983

NA = Not analyzed.

Table B-1
(continued)

Sample		Explosives concentration in soil, ug/g								Date of Analysis
		HMX	RDX	1,3,5-TNB	1,3-DNB	NB	2A-DNT	2,4,6-TNT	2,6-DNT	2,4-DNT
T003	0 - 0.5 ft		33	143			53	128,000		September/October 1983
	0 - 0.5 ft		43	147				118,000		September/October 1983
	0.5 - 1.0 ft			15			14	1,224		February/March 1983
	1.0 - 1.5 ft							796		February/March 1983
	1.5 - 2.0 ft			11				610		February/March 1983
T004	0 - 0.5 ft							64,600		September/October 1983
	0.5 - 1.0 ft			128		26		18,800		September/October 1983
	1.0 - 1.5 ft							1,648		February/March 1983
	1.5 - 2.0 ft							755		February/March 1983
T005	0 - 0.5 ft			33				1,770		September/October 1983
	0.5 - 1.0 ft			72		16	79	17,000		September/October 1983
	1.0 - 1.5 ft			16				1,112		February/March 1983
	1.5 - 2.0 ft							738		February/March 1983
T006	0 - 0.5 ft							534		February/March 1983
	0.5 - 1.0 ft		21	126			26	89,600		September/October 1983
	1.0 - 1.5 ft			23			16	710		February/March 1983
	1.0 - 1.5 ft			18				694		February/March 1983
	1.5 - 2.0 ft			35				5,296		September/October 1983
T007	0 - 0.5 ft							550		February/March 1983
	0.5 - 1.0 ft			10				302		February/March 1983
	1.0 - 1.5 ft							410		February/March 1983
	1.5 - 2.0 ft							534		February/March 1983
T008	0 - 0.5 ft							45		February/March 1983
	0.5 - 1.0 ft							49		February/March 1983
	1.0 - 1.5 ft							1,220		September/October 1983
	1.0 - 1.5 ft							134		September/October 1983
	1.0 - 1.5 ft							108		September/October 1983
	1.0 - 1.5 ft							92		February/March 1983
	1.0 - 1.5 ft							1,304		February/March 1983
	1.0 - 1.5 ft	NA	NA	NA	NA	NA	NA	1,200	NA	NA
	1.0 - 1.5 ft	NA	NA	NA	NA	NA	NA	1,200	NA	NA
	1.5 - 2.0 ft							56		February/March 1983

NA = Not analyzed.

Table B-1
(continued)

Sample	Explosives concentration in soil, ug/g								Date of Analysis
	HMX	RDX	1,3,5-TNB	1,3-DNB	NB	2A-DNT	2,4,6-TNT	2,6-DNT	2,4-DNT
<u>Drain Trough</u>									
W001									
0 - 0.5 ft							120		24
0.5 - 1.0 ft							520		
0.5 - 1.0 ft*							34		
0.5 - 1.0 ft*							54		
0.5 - 1.0 ft*							472		
0.5 - 1.0 ft*							567		
0.5 - 1.0 ft*							524		
0.5 - 1.0 ft*			18				400		
0.5 - 1.0 ft*			38				378		30
W002									
0 - 0.5 ft							424		11
0.5 - 1.0 ft							130		

*The W001 sample was divided into three replicates, which were analyzed a total of seven times.

Table B-2

Soil Samples: Holding Times

Sample	Sample date	Date received at WESTON laboratory	Date drying and sieving completed	Date extraction completed ^a	Holding time (days) ^b
<u>Lagoon No. 1-</u>					
A007	1/25/83	1/27/83	1/31/83	1/31/83	6
A008	1/25/83	1/27/83	1/31/83	1/31/83	6
A017	2/8/83	2/9/83	2/15/83	2/16/83	8
A018	2/8/83	2/9/83	2/15/83	2/16/83	8
A019	1/29/83	2/1/83	2/4/83	2/4/83	6
C013	2/5/83	2/8/83	2/13/83	2/14/83	9
C014	2/5/83	2/8/83	2/13/83	2/14/83	9
C015	1/25/83	1/27/83	1/31/83	2/1/83	7
C016	2/5/83	2/8/83	2/13/83	2/14/83	9
<u>Lagoon No. 2</u>					
A009	1/19/83	1/23/83	2/15/83	--	>27
A012	1/19/83	1/23/83	2/15/83	--	>27
C017	1/20/83	1/23/83	1/26/83	1/26/83	6
C020	1/21/83	1/23/83	1/27/83	1/28/83	7
<u>Lagoon No. 3</u>					
A010	1/21/83	1/23/83	1/27/83	1/28/83	7
A013	1/21/83	1/23/83	1/27/83	1/28/83	7
C018	1/21/83	1/23/83	1/27/83	1/28/83	7
C021	1/21/83	1/23/83	1/28/83	1/28/83	7

Table B-2
(continued)

Sample	Sample date	Date received at WESTON laboratory	Date drying and sieving completed	Date extraction completed ^a	Holding time (days) ^b
<u>Lagoon No. 4</u>					
A011	1/24/83	1/26/83	1/31/83	1/31/83	7
A014	1/24/83	1/26/83	1/31/83	1/31/83	7
C019	1/24/83	1/26/83	1/27/83	1/28/83	4
C022	1/24/83	1/26/83	1/31/83	1/31/83	7
<u>Lagoon No. 5</u>					
A001	1/30/83	2/1/83	2/3/83	2/3/83	4
A003	1/29/83	2/1/83	2/3/83	2/4/83	6
A005	1/29/83	2/1/83	2/4/83	2/4/83	6
A015	1/30/83	2/1/83	2/4/83	2/4/83	5
C001	2/1/83	2/4/83	2/7/83	2/8/83	7
C003	1/30/83	2/1/83	2/3/83	2/3/83	4
C005	2/1/83	2/4/83	2/7/83	2/8/83	7
C007	1/29/83	2/1/83	2/3/83	2/3/83	5
C011	2/1/83	2/4/83	2/7/83	2/8/83	7
<u>Lagoon No. 6</u>					
A002	2/2/83	2/4/83	2/8/83	2/8/83	6
A004	2/3/83	2/7/83	2/10/83	2/10/83	7
A006	2/3/83	2/7/83	2/10/83	2/10/83	7
A016	2/2/83	2/4/83	2/8/83	2/8/83	6
C002 (0-1.0)		2/4/83	2/7/83	2/10/83	2/10/83
6					
C002 (1.0-1.5)	2/4/83	2/7/83	2/10/83	2/14/83	10
C004	2/2/83	2/4/83	2/7/83	2/8/83	6
C006	2/4/83	2/7/83	2/11/83	2/14/83	10
C008	2/3/83	2/7/83	2/10/83	2/10/83	7
C012	2/4/83	2/7/83	2/10/83	2/10/83	6

Table B-2
(continued)

Sample	Sample date	Date received at WESTON laboratory	Date drying and sieving completed	Date extraction completed ^a	Holding time (days) ^b
<u>Overflow Trench</u>					
T001	2/5/83	2/8/83	2/13/83	2/14/83	9
T002	2/5/83	2/8/83	2/13/83	2/15/83	10
T003	2/5/83	2/8/83	2/15/83	2/15/83	10
T004	2/5/83	2/8/83	2/14/83	2/15/83	10
T005	2/5/83	2/8/83	2/14/83	2/15/83	10
T006	2/5/83	2/8/83	2/15/83	2/16/83	11
T007	2/5/83	2/8/83	2/14/83	2/15/83	10
T008	2/5/83	2/8/83	2/12/83	2/15/83	10
<u>Drain Trough</u>					
W001	2/7/83	2/8/83	2/15/83	2/16/83	9
W002	2/7/83	2/8/83	2/15/83	2/16/83	9

^aRefer to last paragraph on page B-1. Some of these extracts were not used for the analyses reported in Table B-1. Those samples for which only September/October results are reported in Table B-1 were re-extracted in September/October, and the new extract was analyzed. In these instances, the holding time is, effectively, 8 months.

^bTarget maximum holding time from date of sampling until completion of extraction was 7 days.

Reference: Draft Final Remedial Investigation for the TNT Washout Facility Lagoons, Site Nos. 21 and 22, Savanna Army Depot Activity (SADA), Savanna, Illinois, Prepared for U.S. Army Toxic and Hazardous Materials Agency, Prepared by Dames and Moore, April 1991.

**DAMES & MOORE**

7101 WISCONSIN AVENUE, SUITE 700, BETHESDA, MARYLAND 20814-4570 (301) 682-1212
TELEX: 318528

December 20, 1990

U.S. Army Toxic and Hazardous
Materials Agency
Building 4480
Aberdeen Proving Ground, Maryland 21010

Attn: CETHA-IR-A/Mr. Pete Rissell

Re: Transmittal of the Analytical Data
for the Samples Collected During
the Lagoon Special Effort (LSE),
Savanna Army Depot Activity (SVADA)
Contract No. DAAA15-88-D-0008
Delivery Order No. 12

Dear Mr. Rissell:

This letter transmits two (2) copies of the analytical data for the soil samples collected during the Lagoon Special Effort (LSE) on December 4, 1990. Attachment A of this letter presents a summary of the analytical results for the soil samples collected during the Lagoon Special Effort (LSE) and Attachment B presents the results of the explosives analysis of these soil samples. The analytical results presented in Attachment B and upon which the assessment presented in Attachment A is based, represent Level 2 data and have not undergone complete quality assurance/quality control review.

As indicated in Attachments A and B, explosives contamination was only detected in one soil sample collected at the Old Lagoons during the LSE--soil sample 312102, collected from the base of the metal-lined wooden drain trough, contained 2,4,6-trinitrotoluene at a concentration of 2.48 ug/g. The results of the nitrate/nitrite analysis of these soil samples and the results of the equipment rinseate blank analyses have not yet been received by Dames & Moore, and will be submitted under separate cover.

As previously discussed, the results of the LSE will be included in an addendum to the "Draft Baseline Risk Assessment for the TNT Washout Facility Lagoons, Site Nos. 21 and 22", to be resubmitted by Dames & Moore to USATHAMA on January 4, 1990 as the "Draft Remedial Investigation for the TNT Washout Facility Lagoons, Site No. 21 and 22" (RI). Addendum A to the Draft RI will include the following parts:

 **DAMES & MOORE**

- Part A: General Operating Information and Operation Instructions for the TNT Washout Facility (Site 1)
- Part B: Supplemental Geological and Hydrogeological Information for the TNT Washout Facility Lagoons (Sites 21 and 22)
- Part C: Ecological Assessment of the TNT Washout Facility Lagoons (Sites 21 and 22)
- Part D: Analytical Results of the Lagoon Special Effort

Part A has been provided to Dames & Moore by Mr. John Clarke of SVADA. This operating information applies to the years 1969 through approximately 1974; operating information is not available for the time period prior to 1969. Part B will provide specific geological and hydrogeological information for Sites 21 and 22 and will supplement the general geological and hydrogeological information presented in the Lagoon BRA. Part C will consist of a desk-top semi-quantitative/qualitative ecological assessment of Sites 21 and 22, based on existing SVADA environmental information. Part D will include the Level 2 results for the LSE--Attachment A and B of this letter, amended to include the nitrate/nitrite analytical results and equipment rinsewater blank analytical results, unavailable at the time of this letter.

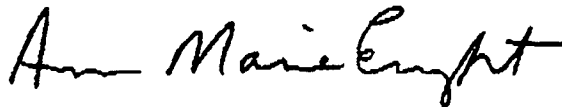
Please contact me if you have any questions.

Sincerely,

DAMES & MOORE



William D. Eaton
Senior Hydrogeologist



Ann Marie Enright
Environmental Engineer

Enclosure

ATTACHMENT A**SUMMARY OF THE ANALYTICAL RESULTS OF THE LAGOON SPECIAL EFFORT**

ATTACHMENT A

SUMMARY OF THE ANALYTICAL RESULTS OF THE LAGOON SPECIAL EFFORT

1.1 INTRODUCTION

This attachment presents the Level 2 analytical results of the soil sampling investigation conducted December 4, 1990 at the Old Lagoons (Site 21) during the Lagoon Special Effort (LSE) at the Savanna Army Depot Activity (SVADA), Savanna, Illinois. The purpose of the LSE was to provide supplemental soil monitoring data requested by EPA Region 5 (hereafter referred to as EPA) to be included as an addendum to the report entitled "Draft Baseline Risk Assessment for the TNT Washout Facility Lagoons, Site Nos. 21 and 22" (Dames & Moore, 1990), hereafter referred to as the draft BRA report. EPA had previously reviewed the draft BRA report and concluded that it would fulfill EPA's RI requirements for Site Nos. 21 and 22 if the additional soil sampling and analysis encompassed by the LSE was conducted, and if the sampling results were attached to the draft BRA report. The draft BRA report written by Dames & Moore for Site Nos. 21 and 22 was not initially intended by USATHAMA to fulfill EPA's RI reporting requirements; however, upon EPA's preliminary review of the draft BRA report, it was concluded to be of sufficient detail to fulfill the RI reporting requirements, pending completion of the LSE. Additionally, implementation of these sampling activities was considered necessary by EPA prior to final approval of the overall SVADA Project Plans.

The following sections discuss the field investigation

program, the chemical analysis program, the chemical analysis results, and an evaluation of the chemical analysis results, followed by the conclusions of the LSE. It should be noted that the analytical results presented herein and upon which this assessment is based, represent Level 2 data, and have not undergone complete quality assurance/quality control review.

1.2 FIELD INVESTIGATION

The field investigation for the LSE involved collection of twenty-two shallow soil samples (312101 through 312122) from a depth interval of zero to 6 inches at the approximate locations indicated in Figure 1. The location of each sample was staked in the field for future surveying. The soil samples were collected to enable an assessment of potential soil contamination beyond the boundaries of the Old Lagoons. Two shallow soil samples were collected along the metal-lined wooden drain trough; fifteen shallow soil samples were collected downgradient of the Old Lagoons; and five shallow soil samples were collected around the other three sides of the Old Lagoons.

The sampling effort also included collection of two equipment rinseate blanks (3R2101R and 3R2102R)--the final "analyte-free" water rinse from equipment cleaning--and two field duplicates (312110D and 312121D).

1.3 CHEMICAL ANALYSIS PROGRAM

Chemical analysis performed on samples collected during the LSE included explosives and nitrate/nitrite. Specific explosive

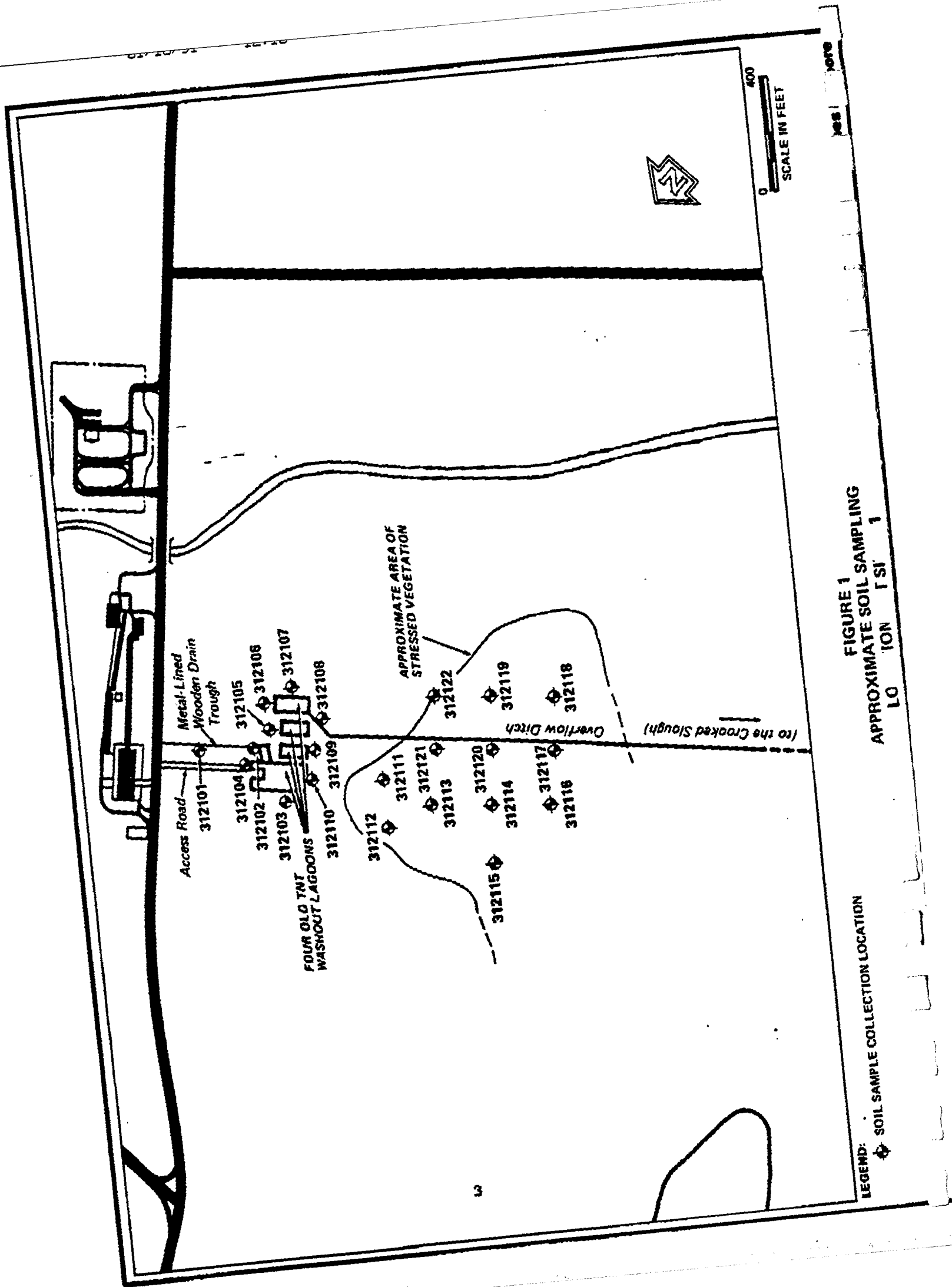


FIGURE 1
APPROXIMATE SOIL SAMPLING
LOCATION

LEGEND: SOIL SAMPLE COLLECTION LOCATION

compounds included: 1,3-dinitrobenzene (DNB), 2,4-dinitrotoluene (DNT), 2,6-DNT, HMX, nitrobenzene, RDX, tetryl, 1,3,5-trinitrobenzene, and 2,4,6-trinitrotoluene (2,4,6-TNT). The rinseates and duplicates were analyzed for the same parameters as the related samples.

Chemical analysis was performed by DataChem Laboratories, Salt Lake City, Utah. Chemical analysis methods are described in Section 7.0 of the Quality Assurance Project Plan (QAPjP), Part C of the SVADA Plans.

1.4 CHEMICAL ANALYSIS RESULTS

The results of the explosives analysis of the soil samples collected during the LSE are presented in Attachment B. The analytical results presented in Attachment B represent Level 2 data and have not undergone complete quality assurance/quality control review. The results of the nitrate/nitrite analysis of these soil samples and the results of the equipment rinseate blank analyses have not yet been received by Dames & Moore and will be forwarded under separate cover.

A review of Attachment B indicates that 2,4,6-TNT was only detected in one soil sample (312102) at a very low concentration (2.48 ug/g). No other explosives were detected in any of the soil samples collected during this investigation.

1.5 EVALUATION OF CHEMICAL ANALYSIS RESULTS

The analytical results indicate that explosives contamination was not detected in the fifteen shallow soil samples collected

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downgradient of the Old Lagoons or in the five shallow soil samples collected around the other three sides of the Old Lagoons.

2,4,6-TNT was detected in one soil sample (312102) collected at the base of the metal-lined wooden drain trough, just prior to its discharge to Lagoon 1, at a low concentration (2.48 ug/g). A comparison of this detected concentration to recommended remedial action criteria developed for 2,4,6-TNT in the Lagoon BRA, indicates that the concentration detected is well below the most stringent of the recommended remedial action criteria (i.e., 17 ug/g for a 10^{-6} carcinogenic risk level).

The concentration of 2,4,6-TNT detected in sample 312102 was significantly less than concentrations of 2,4,6-TNT previously detected by Weston (1984) along the metal-lined wooden drain trough, which ranged up to 567 ug/g. As indicated in the draft BRA report, the concentrations of 2,4,6-TNT detected beneath the drain trough by Weston (1984) were high enough to include this soil within the scope of the selected remedial alternative. The detection of 2,4,6-TNT at a low concentration in sample 312102 does not impact the recommendations of the draft BRA report.

1.6 CONCLUSIONS

Explosives contamination was only detected in one soil sample (312102) collected during the LSE. The concentration of 2,4,6-TNT detected in sample 312102 is well below the most stringent of the remedial action criteria developed in the draft BRA report. Based on the sampling conducted during the LSE and the analytical results presented in the draft BRA report, explosives contamination at the

Old Lagoons appears to be limited to within the lagoons, drain trough, and overflow trench, and does not appear to have migrated downgradient of the lagoons or beyond the perimeter of the bermed areas of the lagoons. Therefore, the results of the LSE confirm that the lateral extent of soil contamination beyond the boundaries of the lagoons is as previously discussed in the draft BRA report for Sites 21 and 22.

ATTACHMENT B**CHEMICAL ANALYSIS RESULTS OF THE LAGOON SPECIAL EFFORT**

ot: Page - 1 Date - 12/19/90

istl Lab Lot No Meth No Units Meas Analyst Class Prime Contr

SV UB MHI LW23 UGG KMS N DM

Sample:

Samp Anal No: 001 File: CQC Site Type:
 Site ID: Field Samp No: Samp Date: / /
 Samp Program: LIT Samp Depth: Samp Tech:
 Lab Samp No: MHI001 Samp Prep Date: 12/06/90 Anal Date: 12/10/90
 Base Closure: N Delivery Order No:

Analysis:

Test Name	Bool	Unc	Mant	Unc	Exp	Dil	Mant	Dil	Exp	Moist	FC	QC	QC	Mant	QC	Exp
135TNB	LT	9.22		-1								M	0.00			0
13DNB	LT	5.04		-1								M	0.00			0
246TNT	LT	2.00		0								M	0.00			0
24DNT	LT	2.50		0								M	0.00			0
26DNT	LT	2.00		0								M	0.00			0
HMX	LT	2.00		0								M	0.00			0
NB	LT	1.14		0								M	0.00			0
RDX	LT	1.28		0								M	0.00			0
TETRYL	LT	2.11		0								M	0.00			0

Sample:

Samp Anal No: 002 File: CQC Site Type:
 Site ID: Field Samp No: Samp Date: / /
 Samp Program: LIT Samp Depth: Samp Tech:
 Lab Samp No: MHI002 Samp Prep Date: 12/06/90 Anal Date: 12/10/90
 Base Closure: N Delivery Order No:

Analysis:

Test Name	Bool	Unc	Mant	Unc	Exp	Dil	Mant	Dil	Exp	Moist	FC	QC	QC	Mant	QC	Exp
135TNB		2.04		0								S	2.50			0
13DNB	LT	5.04		-1								S	0.00			0
246TNT		5.48		0								S	5.00			0
24DNT		4.29		0								S	5.00			0
26DNT	LT	2.00		0								S	0.00			0
HMX	LT	2.00		0								S	0.00			0
NB		4.32		0								S	5.00			0
RDX		3.69		0								S	5.00			0
TETRYL	LT	2.11		0								S	0.00			0

Sample:

Samp Anal No: 003 File: CQC Site Type:
 Site ID: Field Samp No: Samp Date: / /
 Samp Program: LIT Samp Depth: Samp Tech:
 Lab Samp No: MHI003 Samp Prep Date: 12/06/90 Anal Date: 12/10/90
 Base Closure: N Delivery Order No:

Analysis:

Test Name	Bool	Unc	Mant	Unc	Exp	Dil	Mant	Dil	Exp	Moist	FC	QC	QC	Mant	QC	Exp
135TNB		2.27		1								S	2.50			1
13DNB	LT	5.04		-1								S	0.00			0
246TNT		5.22		1								S	5.00			1

* - Indicates that the data is either in error or has not been validated

Lot - Instl: SV Lab: UB Lot No: MHI
 Sample - Sample Analysis No: 003

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Analysis:

Test Name	Bool	Unc Mant	Unc Exp	Dil Mant	Dil Exp	Moist	FC	QC	QC Mant	QC Exp
24DNT		2.26	1					S	2.50	1
26DNT	LT	2.00	0					S	0.00	0
HMX	LT	2.00	0					S	0.00	0
NB		4.79	1					S	5.00	1
RDX		4.33	1					S	5.00	1
TETRYL	LT	2.11	0					S	0.00	0

Sample:

Samp Anal No: 004	File: CQC	Site Type:
Site ID:	Field Samp No:	Samp Date: / /
Samp Program: LIT	Samp Depth:	Samp Tech:
Lab Samp No: MHI004	Samp Prep Date: 12/06/90	Anal Date: 12/10/90
Base Closure: N	Delivery Order No:	

Analysis:

Test Name	Bool	Unc Mant	Unc Exp	Dil Mant	Dil Exp	Moist	FC	QC	QC Mant	QC Exp
135TNB		2.41	1					S	2.50	1
13DNB	LT	5.04	-1					S	0.00	0
246TNT		5.01	1					S	5.00	1
24DNT		2.13	1					S	2.50	1
26DNT	LT	2.00	0					S	0.00	0
HMX	LT	2.00	0					S	0.00	0
NB		4.66	1					S	5.00	1
RDX		4.69	1					S	5.00	1
TETRYL	LT	2.11	0					S	0.00	0

Sample:

Samp Anal No: 005	File: CSO	Site Type: LAGO
Site ID: 312101	Field Samp No:	Samp Date: 12/04/90
Samp Program: C	Samp Depth: 0.0	Samp Tech: U
Lab Samp No: MHI005	Samp Prep Date: 12/06/90	Anal Date: 12/10/90
Base Closure: N	Delivery Order No:	

Analysis:

Test Name	Bool	Unc Mant	Unc Exp	Dil Mant	Dil Exp	Moist	FC	QC	QC Mant	QC Exp
135TNB	LT	9.22	-1						.	
13DNB	LT	5.04	-1						.	
246TNT	LT	2.00	0						.	
24DNT	LT	2.50	0						.	
26DNT	LT	2.00	0						.	
HMX	LT	2.00	0						.	
NB	LT	1.14	0						.	
RDX	LT	1.28	0						.	
TETRYL	LT	2.11	0						.	

* - Indicates that the data is either in error or has not been validated

ot - Instl: SV Lab: UB Lot No: MHI

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Sample:

Samp Anal No: 006 File: CSO Site Type: LAGO
 Site ID: 312102 Field Samp No: Samp Date: 12/04/90
 Samp Program: C Samp Depth: 0.0 Samp Tech: U
 Lab Samp No: MHI006 Samp Prep Date: 12/06/90 Anal Date: 12/10/90
 Base Closure: N Delivery Order No:

Analysis:

Test Name	Bool	Unc Mant	Unc Exp	Dil Mant	Dil Exp	Moist	FC	QC	QC Mant	QC Exp
135TNB	LT	9.22	-1							
13DNB	LT	5.04	-1							
246TNT		2.48	0			17.7				
24DNT	LT	2.50	0							
26DNT	LT	2.00	0							
HMX	LT	2.00	0							
NB	LT	1.14	0							
RDX	LT	1.28	0							
TETRYL	LT	2.11	0							

Sample:

Samp Anal No: 007 File: CSO Site Type: LAGO
 Site ID: 312103 Field Samp No: Samp Date: 12/04/90
 Samp Program: C Samp Depth: 0.0 Samp Tech: U
 Lab Samp No: MHI007 Samp Prep Date: 12/06/90 Anal Date: 12/10/90
 Base Closure: N Delivery Order No:

Analysis:

Test Name	Bool	Unc Mant	Unc Exp	Dil Mant	Dil Exp	Moist	FC	QC	QC Mant	QC Exp
135TNB	LT	9.22	-1							
13DNB	LT	5.04	-1							
246TNT	LT	2.00	0							
24DNT	LT	2.50	0							
26DNT	LT	2.00	0							
HMX	LT	2.00	0							
NB	LT	1.14	0							
RDX	LT	1.28	0							
TETRYL	LT	2.11	0							

Sample:

Samp Anal No: 008 File: CSO Site Type: LAGO
 Site ID: 312104 Field Samp No: Samp Date: 12/04/90
 Samp Program: C Samp Depth: 0.0 Samp Tech: U
 Lab Samp No: MHI008 Samp Prep Date: 12/06/90 Anal Date: 12/10/90
 Base Closure: N Delivery Order No:

Analysis:

Test Name	Bool	Unc Mant	Unc Exp	Dil Mant	Dil Exp	Moist	FC	QC	QC Mant	QC Exp
135TNB	LT	9.22	-1							
13DNB	LT	5.04	-1							
246TNT	LT	2.00	0							
24DNT	LT	2.50	0							
26DNT	LT	2.00	0							
HMX	LT	2.00	0							

* - Indicates that the data is either in error or has not been validated

Lot - Instl: SV Lab: UB Lot No: MHI
 Sample - Sample Analysis No: 008

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Analysis:

Test Name	Bool	Unc Mant	Unc Exp	Dil Mant	Dil Exp	Moist	FC	QC	QC Mant	QC Exp
NB	LT	1.14	0							
RDX	LT	1.28	0							
TETRYL	LT	2.11	0							

Sample:

Samp Anal No: 009	File: CSO	Site Type: LAGO
Site ID: 312105	Field Samp No:	Samp Date: 12/04/90
Samp Program: C	Samp Depth: 0.0	Samp Tech: U
Lab Samp No: MHI009	Samp Prep Date: 12/06/90	Anal Date: 12/10/90
Base Closure: N	Delivery Order No:	

Analysis:

Test Name	Bool	Unc Mant	Unc Exp	Dil Mant	Dil Exp	Moist	FC	QC	QC Mant	QC Exp
135TNB	LT	9.22	-1							
13DNB	LT	5.04	-1							
246TNT	LT	2.00	0							
24DNT	LT	2.50	0							
26DNT	LT	2.00	0							
HMX	LT	2.00	0							
NB	LT	1.14	0							
RDX	LT	1.28	0							
TETRYL	LT	2.11	0							

Sample:

Samp Anal No: 010	File: CSO	Site Type: LAGO
Site ID: 312106	Field Samp No:	Samp Date: 12/04/90
Samp Program: C	Samp Depth: 0.0	Samp Tech: U
Lab Samp No: MHI010	Samp Prep Date: 12/06/90	Anal Date: 12/10/90
Base Closure: N	Delivery Order No:	

Analysis:

Test Name	Bool	Unc Mant	Unc Exp	Dil Mant	Dil Exp	Moist	FC	QC	QC Mant	QC Exp
135TNB	LT	9.22	-1							
13DNB	LT	5.04	-1							
246TNT	LT	2.00	0							
24DNT	LT	2.50	0							
26DNT	LT	2.00	0							
HMX	LT	2.00	0							
NB	LT	1.14	0							
RDX	LT	1.28	0							
TETRYL	LT	2.11	0							

* - Indicates that the data is either in error or has not been validated

Lot - Instl: SV Lab: UB Lot No: MHI

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Sample:

Samp Anal No: 011 File: CSO Site Type: LAGO
 Site ID: 312107 Field Samp No: Samp Date: 12/04/90
 Samp Program: C Samp Depth: 0.0 Samp Tech: U
 Lab Samp No: MHI011 Samp Prep Date: 12/06/90 Anal Date: 12/10/90
 Base Closure: N Delivery Order No:

Analysis:

Test Name	Bool	Unc	Mant	Unc	Exp	Dil	Mant	Dil	Exp	Moist	FC	QC	QC	Mant	QC	Exp
135TNB	LT	9.22		-1												
13DNB	LT	5.04		-1												
246TNT	LT	2.00		0												
24DNT	LT	2.50		0												
26DNT	LT	2.00		0												
HMX	LT	2.00		0												
NB	LT	1.14		0												
RDX	LT	1.28		0												
TETRYL	LT	2.11		0												

Sample:

Samp Anal No: 012 File: CSO Site Type: LAGO
 Site ID: 312108 Field Samp No: Samp Date: 12/04/90
 Samp Program: C Samp Depth: 0.0 Samp Tech: U
 Lab Samp No: MHI012 Samp Prep Date: 12/06/90 Anal Date: 12/10/90
 Base Closure: N Delivery Order No:

Analysis:

Test Name	Bool	Unc	Mant	Unc	Exp	Dil	Mant	Dil	Exp	Moist	FC	QC	QC	Mant	QC	Exp
135TNB	LT	9.22		-1												
13DNB	LT	5.04		-1												
246TNT	LT	2.00		0												
24DNT	LT	2.50		0												
26DNT	LT	2.00		0												
HMX	LT	2.00		0												
NB	LT	1.14		0												
RDX	LT	1.28		0												
TETRYL	LT	2.11		0												

Sample:

Samp Anal No: 013 File: CSO Site Type: LAGO
 Site ID: 312109 Field Samp No: Samp Date: 12/04/90
 Samp Program: C Samp Depth: 0.0 Samp Tech: U
 Lab Samp No: MHI013 Samp Prep Date: 12/06/90 Anal Date: 12/10/90
 Base Closure: N Delivery Order No:

Analysis:

Test Name	Bool	Unc	Mant	Unc	Exp	Dil	Mant	Dil	Exp	Moist	FC	QC	QC	Mant	QC	Exp
135TNB	LT	9.22		-1												
13DNB	LT	5.04		-1												
246TNT	LT	2.00		0												
24DNT	LT	2.50		0												
26DNT	LT	2.00		0												
HMX	LT	2.00		0												

* - Indicates that the data is either in error or has not been validated

Lot - Instl: SV Lab: UB Lot No: MHI
 Sample - Sample Analysis No: 013

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Analysis:

Test Name	Bool	Unc Mant	Unc Exp	Dil Mant	Dil Exp	Moist	FC	QC	QC Mant	QC Exp
NB	LT	1.14	0							
RDX	LT	1.28	0							
TETRYL	LT	2.11	0							

Sample:

Samp Anal No: 014	File: CSO	Site Type: LAGO
Site ID: 312110	Field Samp No:	Samp Date: 12/04/90
Samp Program: C	Samp Depth: 0.0	Samp Tech: U
Lab Samp No: MHI014	Samp Prep Date: 12/06/90	Anal Date: 12/10/90
Base Closure: N	Delivery Order No:	

Analysis:

Test Name	Bool	Unc Mant	Unc Exp	Dil Mant	Dil Exp	Moist	FC	QC	QC Mant	QC Exp
135TNB	LT	9.22	-1							
13DNB	LT	5.04	-1							
246TNT	LT	2.00	0							
24DNT	LT	2.50	0							
26DNT	LT	2.00	0							
HMX	LT	2.00	0							
NB	LT	1.14	0							
RDX	LT	1.28	0							
TETRYL	LT	2.11	0							

Sample:

Samp Anal No: 015	File: CSO	Site Type: LAGO
Site ID: 312111	Field Samp No:	Samp Date: 12/04/90
Samp Program: C	Samp Depth: 0.0	Samp Tech: U
Lab Samp No: MHI015	Samp Prep Date: 12/06/90	Anal Date: 12/10/90
Base Closure: N	Delivery Order No:	

Analysis:

Test Name	Bool	Unc Mant	Unc Exp	Dil Mant	Dil Exp	Moist	FC	QC	QC Mant	QC Exp
135TNB	LT	9.22	-1							
13DNB	LT	5.04	-1							
246TNT	LT	2.00	0							
24DNT	LT	2.50	0							
26DNT	LT	2.00	0							
HMX	LT	2.00	0							
NB	LT	1.14	0							
RDX	LT	1.28	0							
TETRYL	LT	2.11	0							

* - Indicates that the data is either in error or has not been validated

Lot - Instl: SV Lab: UB Lot No: MHI

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Sample:

Samp Anal No: 016 File: CSO Site Type: LAGO
 Site ID: 312112 Field Samp No: Samp Date: 12/04/90
 Samp Program: C Samp Depth: 0.0 Samp Tech: U
 Lab Samp No: MHI016 Samp Prep Date: 12/06/90 Anal Date: 12/10/90
 Base Closure: N Delivery Order No:

Analysis:

Test Name	Bool	Unc Mant	Unc Exp	Dil Mant	Dil Exp	Moist	FC	QC	QC Mant	QC Exp
135TNB	LT	9.22	-1							
13DNB	LT	5.04	-1							
246TNT	LT	2.00	0							
24DNT	LT	2.50	0							
26DNT	LT	2.00	0							
HMX	LT	2.00	0							
NB	LT	1.14	0							
RDX	LT	1.28	0							
TETRYL	LT	2.11	0							

Sample:

Samp Anal No: 017 File: CSO Site Type: LAGO
 Site ID: 312113 Field Samp No: Samp Date: 12/04/90
 Samp Program: C Samp Depth: 0.0 Samp Tech: U
 Lab Samp No: MHI017 Samp Prep Date: 12/06/90 Anal Date: 12/10/90
 Base Closure: N Delivery Order No:

Analysis:

Test Name	Bool	Unc Mant	Unc Exp	Dil Mant	Dil Exp	Moist	FC	QC	QC Mant	QC Exp
135TNB	LT	9.22	-1							
13DNB	LT	5.04	-1							
246TNT	LT	2.00	0							
24DNT	LT	2.50	0							
26DNT	LT	2.00	0							
HMX	LT	2.00	0							
NB	LT	1.14	0							
RDX	LT	1.28	0							
TETRYL	LT	2.11	0							

Sample:

Samp Anal No: 018 File: CSO Site Type: LAGO
 Site ID: 312114 Field Samp No: Samp Date: 12/04/90
 Samp Program: C Samp Depth: 0.0 Samp Tech: U
 Lab Samp No: MHI018 Samp Prep Date: 12/06/90 Anal Date: 12/10/90
 Base Closure: N Delivery Order No:

Analysis:

Test Name	Bool	Unc Mant	Unc Exp	Dil Mant	Dil Exp	Moist	FC	QC	QC Mant	QC Exp
135TNB	LT	9.22	-1							
13DNB	LT	5.04	-1							
246TNT	LT	2.00	0							
24DNT	LT	2.50	0							
26DNT	LT	2.00	0							
HMX	LT	2.00	0							

* - Indicates that the data is either in error or has not been validated

Lot - Instl: SV Lab: UB Lot No: MHI
Sample - Sample Analysis No: 018

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Analysis:

Test Name	Bool	Unc Mant	Unc Exp	Dil Mant	Dil Exp	Moist	FC	QC	QC Mant	QC Exp
NB	LT	1.14	0							
RDX	LT	1.28	0							
TETRYL	LT	2.11	0							

Sample:

Samp Anal No:	019	File:	CSO	Site Type:	LAGO
Site ID:	312115	Field Samp No:		Samp Date:	12/04/90
Samp Program:	C	Samp Depth:	0.0	Samp Tech:	U
Lab Samp No:	MHI019	Samp Prep Date:	12/06/90	Anal Date:	12/10/90
Base Closure:	N	Delivery Order No:			

Analysis:

Test Name	Bool	Unc Mant	Unc Exp	Dil Mant	Dil Exp	Moist	FC	QC	QC Mant	QC Exp
135TNB	LT	9.22	-1							
13DNB	LT	5.04	-1							
246TNT	LT	2.00	0							
24DNT	LT	2.50	0							
26DNT	LT	2.00	0							
HMX	LT	2.00	0							
NB	LT	1.14	0							
RDX	LT	1.28	0							
TETRYL	LT	2.11	0							

Sample:

Samp Anal No:	020	File:	CSO	Site Type:	LAGO
Site ID:	312116	Field Samp No:		Samp Date:	12/04/90
Samp Program:	C	Samp Depth:	0.0	Samp Tech:	U
Lab Samp No:	MHI020	Samp Prep Date:	12/06/90	Anal Date:	12/10/90
Base Closure:	N	Delivery Order No:			

Analysis:

Test Name	Bool	Unc Mant	Unc Exp	Dil Mant	Dil Exp	Moist	FC	QC	QC Mant	QC Exp
135TNB	LT	9.22	-1							
13DNB	LT	5.04	-1							
246TNT	LT	2.00	0							
24DNT	LT	2.50	0							
26DNT	LT	2.00	0							
HMX	LT	2.00	0							
NB	LT	1.14	0							
RDX	LT	1.28	0							
TETRYL	LT	2.11	0							

* - Indicates that the data is either in error or has not been validated

Lot - Instl: SV Lab: UB Lot No: MHI

page - 9 date - 12/19/90

Sample:

Samp Anal No: 021 File: CSO Site Type: LAGO
 Site ID: 312110D Field Samp No: Samp Date: 12/04/90
 Samp Program: C Samp Depth: 0.0 Samp Tech: U
 Lab Samp No: MHI021 Samp Prep Date: 12/06/90 Anal Date: 12/10/90
 Base Closure: N Delivery Order No:

Analysis:

Test Name	Bool	Unc	Mant	Unc	Exp	Dil	Mant	Dil	Exp	Moist	FC	QC	QC	Mant	QC	Exp
135TNB	LT	9.22		-1							D		.			
13DNB	LT	5.04		-1							D		.			
246TNT	LT	2.00		0							D		.			
24DNT	LT	2.50		0							D		.			
26DNT	LT	2.00		0							D		.			
HMX	LT	2.00		0							D		.			
NB	LT	1.14		0							D		.			
RDX	LT	1.28		0							D		.			
TETRYL	LT	2.11		0							D		.			

Sample:

Samp Anal No: 022 File: CSO Site Type: LAGO
 Site ID: 312117 Field Samp No: Samp Date: 12/04/90
 Samp Program: C Samp Depth: 0.0 Samp Tech: U
 Lab Samp No: MHI022 Samp Prep Date: 12/06/90 Anal Date: 12/10/90
 Base Closure: N Delivery Order No:

Analysis:

Test Name	Bool	Unc	Mant	Unc	Exp	Dil	Mant	Dil	Exp	Moist	FC	QC	QC	Mant	QC	Exp
135TNB	LT	9.22		-1									.			
13DNB	LT	5.04		-1									.			
246TNT	LT	2.00		0									.			
24DNT	LT	2.50		0									.			
26DNT	LT	2.00		0									.			
HMX	LT	2.00		0									.			
NB	LT	1.14		0									.			
RDX	LT	1.28		0									.			
TETRYL	LT	2.11		0									.			

Sample:

Samp Anal No: 023 File: CSO Site Type: LAGO
 Site ID: 312118 Field Samp No: Samp Date: 12/04/90
 Samp Program: C Samp Depth: 0.0 Samp Tech: U
 Lab Samp No: MHI023 Samp Prep Date: 12/06/90 Anal Date: 12/10/90
 Base Closure: N Delivery Order No:

Analysis:

Test Name	Bool	Unc	Mant	Unc	Exp	Dil	Mant	Dil	Exp	Moist	FC	QC	QC	Mant	QC	Exp
135TNB	LT	9.22		-1									.			
13DNB	LT	5.04		-1									.			
246TNT	LT	2.00		0									.			
24DNT	LT	2.50		0									.			
26DNT	LT	2.00		0									.			
HMX	LT	2.00		0									.			

* - Indicates that the data is either in error or has not been validated

Lot - Instl: SV Lab: UB Lot No: MHI
 Sample - Sample Analysis No: 023

page - 10 date - 12/19/90

Analysis:

Test Name	Bool	Unc Mant	Unc Exp	Dil Mant	Dil Exp	Moist	FC	QC	QC Mant	QC Exp
NB	LT	1.14	0							
RDX	LT	1.28	0							
TETRYL	LT	2.11	0							

Sample:

Samp Anal No: 024	File: CSO	Site Type: LAGO
Site ID: 312119	Field Samp No:	Samp Date: 12/04/90
Samp Program: C	Samp Depth: 0.0	Samp Tech: U
Lab Samp No: MHI024	Samp Prep Date: 12/06/90	Anal Date: 12/10/90
Base Closure: N	Delivery Order No:	

Analysis:

Test Name	Bool	Unc Mant	Unc Exp	Dil Mant	Dil Exp	Moist	FC	QC	QC Mant	QC Exp
135TNB	LT	9.22	-1							
13DNB	LT	5.04	-1							
246TNT	LT	2.00	0							
24DNT	LT	2.50	0							
26DNT	LT	2.00	0							
HMX	LT	2.00	0							
NB	LT	1.14	0							
RDX	LT	1.28	0							
TETRYL	LT	2.11	0							

Sample:

Samp Anal No: 025	File: CSO	Site Type: LAGO
Site ID: 312120	Field Samp No:	Samp Date: 12/04/90
Samp Program: C	Samp Depth: 0.0	Samp Tech: U
Lab Samp No: MHI025	Samp Prep Date: 12/06/90	Anal Date: 12/10/90
Base Closure: N	Delivery Order No:	

Analysis:

Test Name	Bool	Unc Mant	Unc Exp	Dil Mant	Dil Exp	Moist	FC	QC	QC Mant	QC Exp
135TNB	LT	9.22	-1							
13DNB	LT	5.04	-1							
246TNT	LT	2.00	0							
24DNT	LT	2.50	0							
26DNT	LT	2.00	0							
HMX	LT	2.00	0							
NB	LT	1.14	0							
RDX	LT	1.28	0							
TETRYL	LT	2.11	0							

* - Indicates that the data is either in error or has not been validated

Lot - Instl: SV Lab: UB Lot No: MHI

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Sample:

Samp Anal No: 026 File: CSO Site Type: LAGO
 Site ID: 312121 Field Samp No: Samp Date: 12/04/90
 Samp Program: C Samp Depth: 0.0 Samp Tech: U
 Lab Samp No: MHI026 Samp Prep Date: 12/06/90 Anal Date: 12/10/90
 Base Closure: N Delivery Order No:

Analysis:

Test Name	Bool	Unc Mant	Unc Exp	Dil Mant	Dil Exp	Moist	FC	QC	QC	Mant	QC	Exp
135TNB	LT	9.22	-1									
13DNB	LT	5.04	-1									
246TNT	LT	2.00	0									
24DNT	LT	2.50	0									
26DNT	LT	2.00	0									
HMX	LT	2.00	0									
NB	LT	1.14	0									
RDX	LT	1.28	0									
TETRYL	LT	2.11	0									

Sample:

Samp Anal No: 027 File: CSO Site Type: LAGO
 Site ID: 312121D Field Samp No: Samp Date: 12/04/90
 Samp Program: C Samp Depth: 0.0 Samp Tech: U
 Lab Samp No: MHI027 Samp Prep Date: 12/06/90 Anal Date: 12/10/90
 Base Closure: N Delivery Order No:

Analysis:

Test Name	Bool	Unc Mant	Unc Exp	Dil Mant	Dil Exp	Moist	FC	QC	QC	Mant	QC	Exp
135TNB	LT	9.22	-1				D					
13DNB	LT	5.04	-1				D					
246TNT	LT	2.00	0				D					
24DNT	LT	2.50	0				D					
26DNT	LT	2.00	0				D					
HMX	LT	2.00	0				D					
NB	LT	1.14	0				D					
RDX	LT	1.28	0				D					
TETRYL	LT	2.11	0				D					

Sample:

Samp Anal No: 028 File: CSO Site Type: LAGO
 Site ID: 312122 Field Samp No: Samp Date: 12/04/90
 Samp Program: C Samp Depth: 0.0 Samp Tech: U
 Lab Samp No: MHI028 Samp Prep Date: 12/06/90 Anal Date: 12/10/90
 Base Closure: N Delivery Order No:

Analysis:

Test Name	Bool	Unc Mant	Unc Exp	Dil Mant	Dil Exp	Moist	FC	QC	QC	Mant	QC	Exp
135TNB	LT	9.22	-1									
13DNB	LT	5.04	-1									
246TNT	LT	2.00	0									
24DNT	LT	2.50	0									
26DNT	LT	2.00	0									
HMX	LT	2.00	0									

* - Indicates that the data is either in error or has not been validated

ot - Instl: SV Lab: UB Lot No: MHI
ample - Sample Analysis No: 028

page - 12 date - 12/19/90

Analysis:

Test Name	Bool	Unc	Mant	Unc	Exp	Dil	Mant	Dil	Exp	Moist	FC	QC	QC	Mant	QC	Exp
NB	LT	1.14			0											
RDX	LT	1.28			0											
TETRYL	LT	2.11			0											

Sample:

Samp Anal No:	029	File:	CQC	Site Type:	
Site ID:		Field Samp No:		Samp Date:	/ /
Samp Program:	LIT	Samp Depth:		Samp Tech:	
Lab Samp No:	MHI029	Samp Prep Date:	12/06/90	Anal Date:	12/10/90
Base Closure:	N	Delivery Order No:			

Analysis:

Test Name	Bool	Unc	Mant	Unc	Exp	Dil	Mant	Dil	Exp	Moist	FC	QC	QC	Mant	QC	Exp
135TNB		1.81			2							S	2.00			2
246TNT		3.73			2							S	4.00			2
24DNT		1.68			2							S	2.00			2
NB		3.64			2							S	4.00			2
RDX		3.47			2							S	4.00			2

* - Indicates that the data is in error or that it has not been validated

APPENDIX D

SAMPLING METHODS*

- S007
- M1
- M2
- M3
- M5
- M8
- MM0010
- Multi-metals

***Modifications to Standard Methods are Summarized on Table D-1.**



Table D-1

Modifications to Sampling Methods

Method Number	Modification
5	Combined EPA 5 and 8 test trains
8	Only sulfur dioxide will be determined. The isopropanol impinger will be included, however, it will not be analyzed.
Multi-metals	A revised draft version may be available within the next year. WESTON plans to adhere to the updated version.
Method 0010	<p>Two XAD-2 resin tubes (each containing 40 grams of resin) will be used in series.</p> <p>WESTON will use 50% methylene chloride and 50% acetone as the recovery solvent instead of the methylene chloride/methanol mix.</p> <p>All test train components will be composited and explosives will be analyzed and reported on a total test train basis.</p>

METHOD S007



Method Number: S007
Method Name: Trowel and Scoop
Basic Method: Solid Grab Sample
Matrix: Solids
Apparatus: Stainless steel laboratory scoop
(7 x 15 cm).

Sampling Method Parameters:

Prior to collecting a sample, the top half-inch of the solid must be removed. Kg-sized samples are obtained by combining subsamples taken at several locations.

References: U.S. Environmental Protection Agency/Office of Solid Waste, Washington, D.C., "Test Methods for Evaluating Solid Waste - Physical/Chemical Methods," SW 846 (1980).

DeVera, E.R., B.P. Simmons, R.D. Stephens, and D.L. Strom, "Samplers and Sampling Procedures for Hazardous Waste Streams," EPA-600/2-80-018 (January 1980). NTIS No. PB80-135353.

METHOD 1

Sample and Velocity Traverses
for Stationary Sources

METHOD 1—SAMPLE AND VELOCITY TRAVERSES FOR STATIONARY SOURCES

1. Principle and Applicability

1.1 Principle. To aid in the representative measurement of pollutant emissions and/or total volumetric flow rate from a stationary source, a measurement site where the effluent stream is flowing in a known direction is selected, and the cross-section of the stack is divided into a number of equal areas. A traverse point is then located within each of these equal areas.

1.2 Applicability. This method is applicable to flowing gas streams in ducts, stacks, and flues. The method cannot be used when: (1) flow is cyclonic or swirling (see Section 2.4), (2) a stack is smaller than about 0.30 meter (12 in.) in diameter, or 0.071 m² (113 in.²) cross-sectional area, or (3) the measurement site is less than two stack or duct diameters downstream or less than a half diameter upstream from a flow disturbance.

The requirements of this method must be considered before construction of a new facility from which emissions will be measured; failure to do so may require subsequent alterations to the stack or deviation from the standard procedure. Cases involving variants are subject to approval by the Administrator, U.S. Environmental Protection Agency.

2. Procedure

2.1 Selection of Measurement Site. Sampling or velocity measurement is performed at a site located at least eight stack or duct diameters downstream and two diameters upstream from any flow disturbance such as a bend, expansion, or contraction in the stack, or from a visible flame. If necessary, an alternative location may be selected, at a position at least two stack or duct diameters downstream and a half diameter upstream from any flow disturbance. For a rectangular cross section, an equivalent diameter (D_e) shall be calculated from the following equation, to determine the upstream and downstream distances:

$$D_e = \frac{2LW}{(L+W)}$$

where L = length and W = width.

An alternative procedure is available for determining the acceptability of a measurement location not meeting the criteria above. This procedure, determination of gas flow angles at the sampling points and comparing the results with acceptability criteria, is described in Section 2.5.

2.2 Determining the Number of Traverse Points.

2.2.1 Particulate Traverses. When the eight- and two-diameter criterion can be met, the minimum number of traverse points shall be: (1) twelve, for circular or rectangular stacks with diameters (or equivalent diameters) greater than 0.61 meter (24 in.); (2) eight, for circular stacks with diameters between 0.30 and 0.61 meter (12-24 in.); (3) nine, for rectangular stacks with equivalent diameters between 0.30 and 0.61 meter (12-24 in.).

When the eight- and two-diameter criterion cannot be met, the minimum number of traverse points is determined from Figure 1-1. Before referring to the figure, however, determine the distances from the chosen

measurement site to the nearest upstream and downstream disturbances, and divide each distance by the stack diameter or equivalent diameter, to determine the distance in terms of the number of duct diameters. Then, determine from Figure 1-1 the minimum number of traverse points that corresponds: (1) to the number of duct diameters upstream; and (2) to the number of diameters downstream. Select the higher of the two minimum numbers of traverse points, or a greater value, so that for circular stacks the number is a multiple of 4, and for rectangular stacks, the number is one of those shown in Table 1-1.

TABLE 1-1. CROSS-SECTION LAYOUT FOR RECTANGULAR STACKS

Number of traverse points	Matrix layout
9	3x3
12	4x3
16	4x4
20	5x4
25	5x5
30	6x5
36	6x6
42	7x6
49	7x7

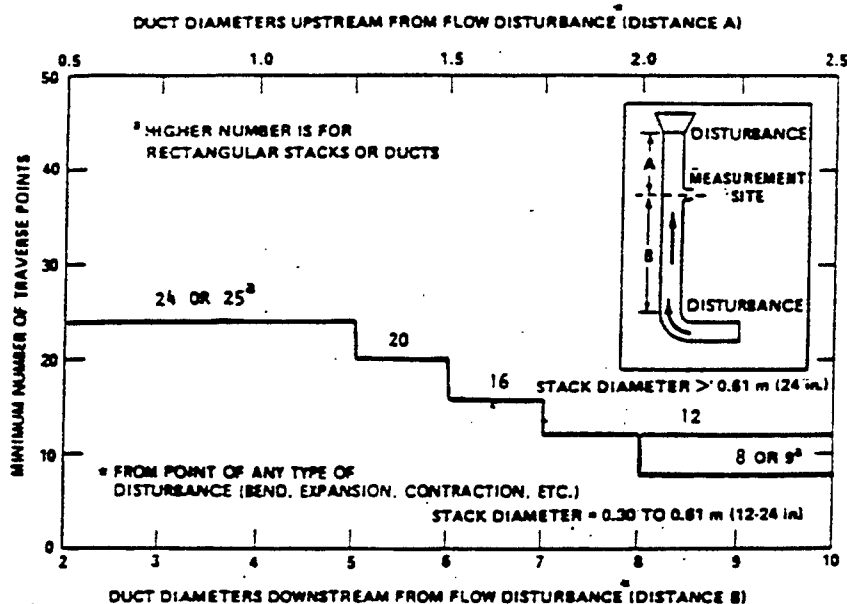


Figure 1-1. Minimum number of traverse points for particulate traverses.

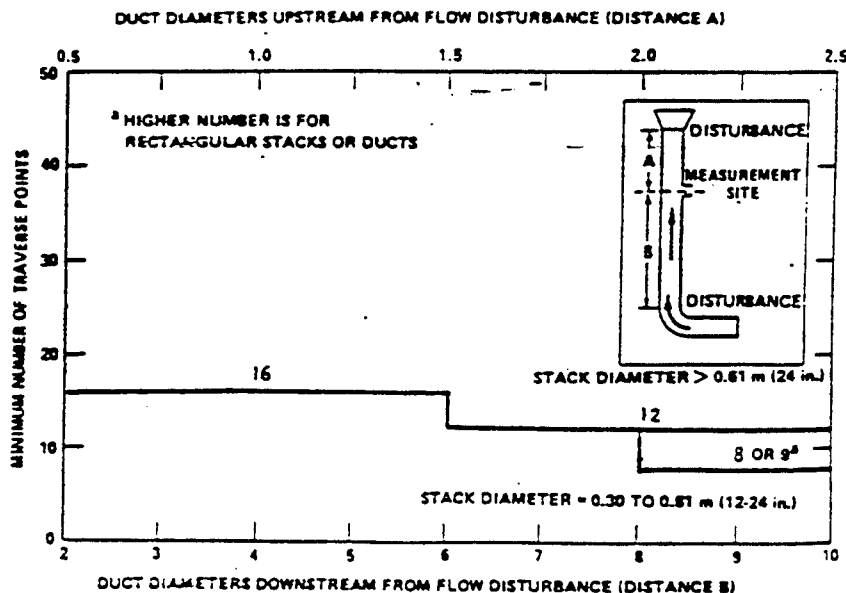


Figure 1-2. Minimum number of traverse points for velocity (nonparticulate) traverses.

2.2.2 Velocity (Non-Particulate) Traverses. When velocity or volumetric flow rate is to be determined (but not particulate matter), the same procedure as that for particulate traverses (Section 2.2.1) is followed, except that Figure 1-2 may be used instead of Figure 1-1.

2.3 Cross-sectional Layout and Location of Traverse Points.

2.3.1 Circular Stacks. Locate the traverse points on two perpendicular diameters according to Table 1-2 and the example shown in Figure 1-3. Any equation (for examples, see Citations 2 and 3 in the Bibliography) that gives the same values as those in Table 1-2 may be used in lieu of Table 1-2.

For particulate traverses, one of the diameters must be in a plane containing the greatest expected concentration variation, e.g., after bends, one diameter shall be in the plane of the bend. This requirement becomes less critical as the distance from the disturbance increases; therefore, other diameter locations may be used, subject to approval of the Administrator.

In addition for stacks having diameters greater than 0.61 m (24 in.) no traverse points shall be located within 2.5 centimeters (1.00 in.) of the stack walls; and for stack diameters equal to or less than 0.61 m (24 in.), no traverse points shall be located within 1.3 cm (0.50 in.) of the stack walls.

To meet these criteria, observe the procedures given below.

2.3.1.1 Stacks With Diameters Greater Than 0.61 m (24 in.). When any of the traverse points as located in Section 2.3.1 fall within 2.5 cm (1.00 in.) of the stack walls, relocate them away from the stack walls to: (1) a distance of 2.5 cm (1.00 in.); or (2) a distance equal to the nozzle inside diameter, whichever is larger. These relocated traverse points (on each end of a diameter) shall be the "adjusted" traverse points.

Whenever two successive traverse points are combined to form a single adjusted traverse point, treat the adjusted point as two separate traverse points, both in the sampling (or velocity measurement) procedure, and in recording the data.

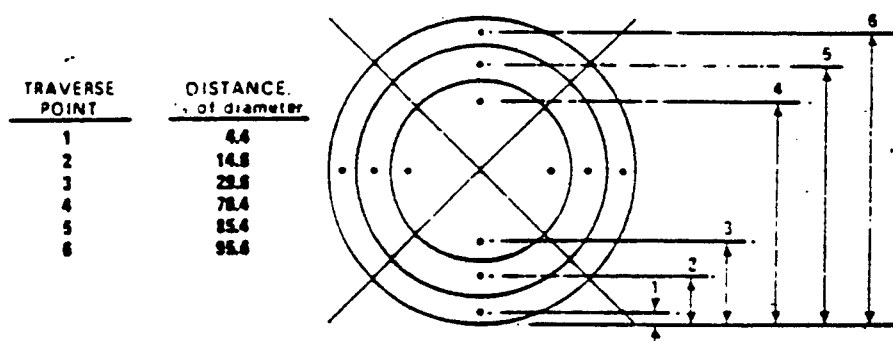


Figure 1-3. Example showing circular stack cross section divided into 12 equal areas, with location of traverse points indicated.

TABLE 1-2. LOCATION OF TRAVERSE POINTS IN CIRCULAR STACKS

(Percent of stack diameter from inside wall to traverse point)

Traverse point number on a diameter	Number of traverse points on a diameter—											
	2	4	6	8	10	12	14	16	18	20	22	24
1	14.8	6.7	4.4	3.2	2.6	2.1	1.8	1.6	1.4	1.3	1.1	1.1
2	29.8	14.8	10.5	8.2	6.7	5.7	4.9	4.4	3.9	3.5	3.2	3.2
3	44.4	29.8	19.4	14.6	11.8	9.9	8.5	7.5	6.7	6.0	5.5	5.5
4	58.4	44.4	32.3	22.6	17.7	14.6	12.5	10.9	9.7	8.7	7.9	7.9
5	71.4	58.4	44.4	34.2	25.0	20.1	16.9	14.6	12.9	11.6	10.5	10.5
6	83.3	71.4	58.4	44.4	35.6	26.9	22.0	18.8	16.5	14.6	13.2	13.2
7	94.3	83.3	71.4	58.4	44.4	36.6	28.3	23.6	20.4	18.0	16.1	16.1
8		94.3	83.3	71.4	58.4	44.4	37.5	29.6	25.0	21.8	19.4	19.4
9			94.3	83.3	71.4	58.4	44.4	38.2	30.6	26.2	23.0	23.0
10				94.3	83.3	71.4	58.4	44.4	38.8	31.5	27.2	27.2
11					94.3	83.3	71.4	58.4	44.4	39.3	32.3	32.3
12						94.3	83.3	71.4	58.4	44.4	39.3	39.3
13							94.3	83.3	71.4	58.4	44.4	44.4
14								94.3	83.3	71.4	58.4	58.4
15									94.3	83.3	71.4	71.4
16										94.3	83.3	83.3
17											94.3	94.3
18												94.3
19												
20												
21												
22												
23												
24												

2.3.1.2 Stacks With Diameters Equal to or Less Than 0.61 m (24 in.). Follow the procedure in Section 2.3.1.1, noting only that any "adjusted" points should be relocated away from the stack walls to: (1) a distance of 1.3 cm (0.50 in.); or (2) a distance equal to the nozzle inside diameter, whichever is larger.

2.3.2 Rectangular Stacks. Determine the number of traverse points as explained in Sections 2.1 and 2.2 of this method. From Table 1-1, determine the grid configuration. Divide the stack cross-section into as many equal rectangular elemental areas as traverse points, and then locate a traverse point at the centroid of each equal area according to the example in Figure 1-4.

If the tester desires to use more than the minimum number of traverse points, expand the "minimum number of traverse points" matrix (see Table 1-1) by adding the extra traverse points along one or the other or both legs of the matrix; the final matrix need not be balanced. For example, if a 4x3 "minimum number of points" matrix were expanded to 36 points, the final matrix could be 9x4 or 12x3, and would not necessarily have to be 6x6. After constructing the final matrix, divide the stack cross-section into as many equal rectangular, elemental areas as traverse points, and locate a traverse point at the centroid of each equal area.

The situation of traverse points being too close to the stack walls is not expected to arise with rectangular stacks. If this problem should ever arise, the Administrator must be contacted for resolution of the matter.

2.4 Verification of Absence of Cyclonic Flow. In most stationary sources, the direction of stack gas flow is essentially parallel to the stack walls. However, cyclonic flow may exist (1) after such devices as cyclones and inertial demisters following venturi scrubbers, or (2) in stacks having tangential inlets or other duct configurations which tend to induce swirling; in these instances, the presence or absence of cyclonic flow at the sampling location must be determined. The following techniques are acceptable for this determination.

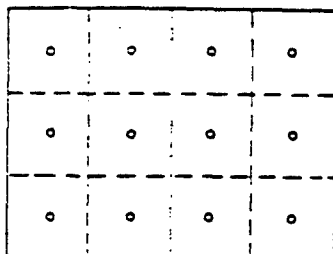


Figure 1-4. Example showing rectangular stack cross section divided into 12 equal areas, with a traverse point at centroid of each area.

Level and zero the manometer. Connect a Type S pitot tube to the manometer. Position the Type S pitot tube at each traverse point, in succession, so that the planes of the face openings of the pitot tube are perpendicular to the stack cross-sectional plane; when the Type S pitot tube is in this position, it is at "0" reference." Note the differential pressure (Δp) reading at each traverse point. If a null (zero) pitot reading is obtained at 0° reference at a given traverse point, an acceptable flow condition exists at that point. If the pitot reading is not zero at 0° reference, rotate the pitot tube (up to $\pm 90^\circ$ yaw angle), until a null reading is obtained. Carefully determine and record the value of the rotation angle (α) to the nearest degree. After the null technique has been applied at each traverse point, calculate the average of the absolute values of α ; assign α values of 0° to those points for which no rotation was required, and include these in the overall average. If the average value of α is greater than 20°, the overall flow condition in the stack is unacceptable and alternative methodology, subject to the approval of the Administrator, must be used to perform accurate sample and velocity traverses.

The alternative procedure described in Section 2.5 may be used to determine the rotation angles in lieu of the procedure described above. The limit of acceptability for the average value of α would remain 20°.

2.5 Alternative Measurement Site Selection Procedure. This alternative applies to sources where measurement locations are less than 2 equivalent stack or duct diameters downstream or less than $\frac{1}{4}$ duct diameter upstream from a flow disturbance. The alternative should be limited to ducts larger than 24 in. in diameter where blockage and wall effects are minimal. A directional flow-sensing probe is used to measure pitch and yaw angles of the gas flow at 40 or more traverse points; the resultant angle is calculated and compared with acceptable criteria for mean and standard deviation.

Note.—Both the pitch and yaw angles are measured from a line passing through the traverse point and parallel to the stack axis. The pitch angle is the angle of the gas flow component in the plane that INCLUDES the traverse line and is parallel to the stack axis. The yaw angle is the angle of the gas flow component in the plane PERPENDICULAR to the traverse line at the traverse point and is measured from the line passing through the traverse point and parallel to the stack axis.

2.5.1 Apparatus.

2.5.1.1 Directional Probe. Any directional probe, such as United Sensor Type DA Three-Dimensional Directional Probe, capable of measuring both the pitch and yaw angles of gas flows is acceptable. (Note: Mention of trade name or specific products does not constitute endorsement by the U.S. Environmental Protection Agency.) Assign an identification number to the directional

probe, and permanently mark or engrave the number on the body of the probe. The pressure holes of directional probes are susceptible to plugging when used in particulate-laden gas streams. Therefore, a system for cleaning the pressure holes by "back-purging" with pressurized air is required.

2.5.1.2 Differential Pressure Gauges. Inclined manometers, U-tube manometers, or other differential pressure gauges (e.g., magnetic gauges) that meet the specifications described in Method 2, § 2.2.

Note.—If the differential pressure gauge produces both negative and positive readings, then both negative and positive pressure readings shall be calibrated at a minimum of three points as specified in Method 2, § 2.2.

2.5.2 Traverse Points. Use a minimum of 40 traverse points for circular ducts and 42 points for rectangular ducts for the gas flow angle determinations. Follow § 2.3 and Table 1-1 or 1-2 for the location and layout of the traverse points. If the measurement location is determined to be acceptable according to the criteria in this alternative procedure, use the same traverse point number and locations for sampling and velocity measurements.

2.5.3 Measurement Procedure.

2.5.3.1 Prepare the directional probe and differential pressure gauges as recommended by the manufacturer. Capillary tubing or surge tanks may be used to dampen pressure fluctuations. It is recommended, but not required, that a pretest leak check be conducted. To perform a leak check, pressurize or use suction on the impact opening until a reading of at least 7.5 cm (3 in.) H₂O registers on the differential pressure gauge, then plug the impact opening. The pressure of a leak-free system will remain stable for at least 15 seconds.

2.5.3.2 Level and zero the manometers. Since the manometer level and zero may drift because of vibrations and temperature changes, periodically check the level and zero during the traverse.

2.5.3.3 Position the probe at the appropriate locations in the gas stream, and rotate until zero deflection is indicated for the yaw angle pressure gauge. Determine and record the yaw angle. Record the pressure gauge readings for the pitch angle, and determine the pitch angle from the calibration curve. Repeat this procedure for each traverse point. Complete a "back-purge" of the pressure lines and the impact openings prior to measurements of each traverse point.

A post-test check as described in § 2.5.3.1 is required. If the criteria for a leak-free system are not met, repair the equipment, and repeat the flow angle measurements.

2.5.4 Calculate the resultant angle at each traverse point, the average resultant angle, and the standard deviation using the following equations. Complete the calculations retaining at least one extra significant figure beyond that of the acquired data. Round the values after the final calculations.

2.5.4.1 Calculate the resultant angle at each traverse point:
 $R_i = \arccosine [(\cosine Y_i) (\cosine P_i)]$ Eq. 1-2

Where:
 R = Resultant angle at traverse point i , degree.
 Y_i = Yaw angle at traverse point i , degree.
 P_i = Pitch angle at traverse point i , degree.

2.5.4.2 Calculate the average resultant for the measurements:

$$\bar{R} = \frac{\sum R_i}{n} \quad \text{Eq. 1-3}$$

where:
 \bar{R} = Average resultant angle, degree.
 n = Total number of traverse points.

2.5.4.3 Calculate the standard deviations:

$$S_d = \sqrt{\frac{\sum_{i=1}^n (R_i - \bar{R})^2}{(n-1)}} \quad \text{Eq. 1-4}$$

Where:
 S_d = Standard deviation, degrees.

2.5.5 The measurement location is acceptable if $\bar{R} < 20^\circ$ and $S_d < 10^\circ$.

2.5.6 Calibration. Use a flow system as described in Sections 4.1.2.1 and 4.1.2.2 of Method 2. In addition, the flow system shall have the capacity to generate two test-section velocities: one between 365 and 730 m/min (1200 and 2400 ft/min) and one between 730 and 1100 m/min (2400 and 3600 ft/min).

2.5.6.1 Cut two entry ports in the test section. The axes through the entry ports shall be perpendicular to each other and intersect in the centroid of the test section. The ports should be elongated slots parallel to the axis of the test section and of sufficient length to allow measurement of pitch angles while maintaining the pitot head position at the test-section centroid. To facilitate alignment of the directional probe during calibration, the test section should be constructed of plexiglass or some other transparent material. All calibration measurements should be made at the same point in the test section, preferably at the centroid of the test-section.

2.5.6.2 To ensure that the gas flow is parallel to the central axis of the test section, follow the procedure in Section 2.4 for cyclonic flow determination to measure the gas flow angles at the centroid of the test section from two test ports located 90° apart. The gas flow angle measured in each port must be $\pm 2^\circ$ of 0° . Straightening vanes should be installed, if necessary, to meet this criterion.

2.5.6.3 Pitch Angle Calibration. Perform a calibration traverse according to the manufacturer's recommended protocol in 5° increments for angles from -60° to $+60^\circ$ at one velocity in each of the two ranges

specified above. Average the pressure ratio values obtained for each angle in the two flow ranges, and plot a calibration curve with the average values of the pressure ratio (or other suitable measurement factor as recommended by the manufacturer) versus the pitch angle. Draw a smooth line through the data points. Plot also the data values for each traverse point. Determine the differences between the measured data values and the angle from the calibration curve at the same pressure ratio. The difference at each comparison must be within 2° for angles between 0° and 40° and within 3° for angles between 40° and 60° .

2.5.6.4 Yaw Angle Calibration. Mark the three-dimensional probe to allow the determination of the yaw position of the probe. This is usually a line extending the length of the probe and aligned with the impact opening. To determine the accuracy of measurements of the yaw angle, only the zero or null position need be calibrated as follows. Place the directional probe in the test section, and rotate the probe until the zero position is found. With a protractor or other angle measuring device, measure the angle indicated by the yaw angle indicator on the three-dimensional probe. This should be within 2° of 0° . Repeat this measurement for any other points along the length of the pitot where yaw angle measurements could be read in order to account for variations in the pitot markings used to indicate pitot head positions.

3. Bibliography

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METHOD 2

Determination of Stack Gas Velocity
and Volumetric Flow Rate

METHOD 2—DETERMINATION OF STACK GAS VELOCITY AND VOLUMETRIC FLOW RATE (TYPE S PITOT TUBE)

1. Principle and Applicability

1.1 Principle. The average gas velocity in a stack is determined from the gas density and from measurement of the average velocity head with a Type S (Staustscheibe or reverse type) pitot tube.

1.2 Applicability. This method is applicable for measurement of the average velocity of a gas stream and for quantifying gas flow.

This procedure is not applicable at measurement sites which fail to meet the criteria of Method 1, Section 2.1. Also, the method cannot be used for direct measurement in cyclonic or swirling gas streams; Section 2.4 of Method 1 shows how to determine cyclonic or swirling flow conditions. When unacceptable conditions exist, alternative procedures, subject to the approval of the Administrator, U.S. Environmental Protection Agency, must be employed to make accurate flow rate determinations; examples of such alternative procedures are: (1) to install straightening vanes; (2) to calculate the total volumetric flow rate stoichiometrically, or (3) to move to another measurement site at which the flow is acceptable.

2. Apparatus

Specifications for the apparatus are given below. Any other apparatus that has been demonstrated (subject to approval of the Administrator) to be capable of meeting the specifications will be considered acceptable.

2.1 Type S Pitot Tube. The Type S pitot tube (Figure 2-1) shall be made of metal tubing (e.g. stainless steel). It is recommended that the external tubing diameter (dimension D, Figure 2-2b) be between 0.48 and 0.95 centimeters ($\frac{1}{8}$ and $\frac{3}{16}$ inch). There shall be an equal distance from the base of each leg of the pitot tube to its face-opening plane (dimensions P_1 and P_2 , Figure 2-2b); it is recommended that this distance be between 1.05 and 1.50 times the external tubing diameter. The face openings of the pitot tube shall, preferably, be aligned as shown in Figure 2-2; however, slight misalignments of the openings are permissible (see Figure 2-3).

The Type S pitot tube shall have a known coefficient, determined as outlined in Section 4. An identification number shall be assigned to the pitot tube; this number shall be permanently marked or engraved on the body of the tube.

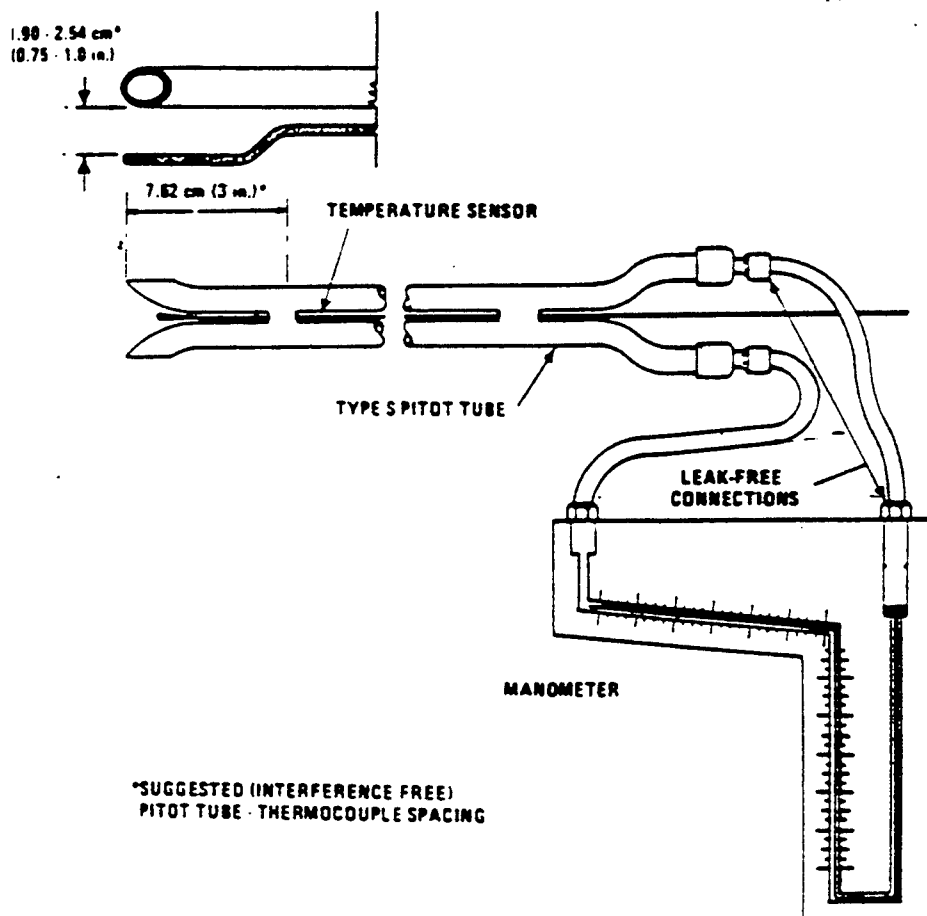


Figure 2-1. Type S pitot tube manometer assembly.

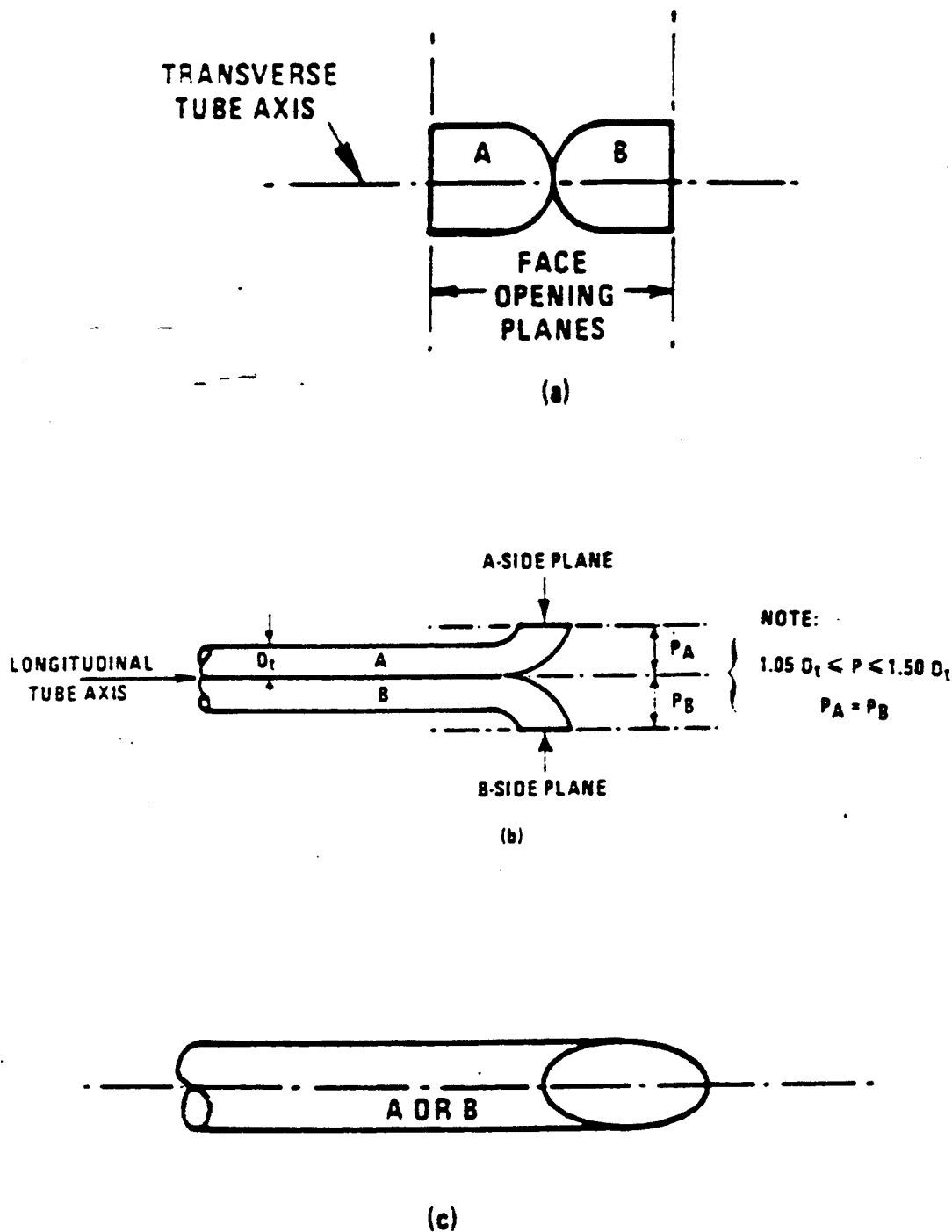


Figure 2-2. Properly constructed Type S pitot tube, shown in: (a) end view, face opening planes perpendicular to transverse axis; (b) top view, face opening planes parallel to longitudinal axis; (c) side view, both legs of equal length and centerlines coincident, when viewed from both sides. Baseline coefficient values of 0.84 may be assigned to pitot tubes constructed this way.

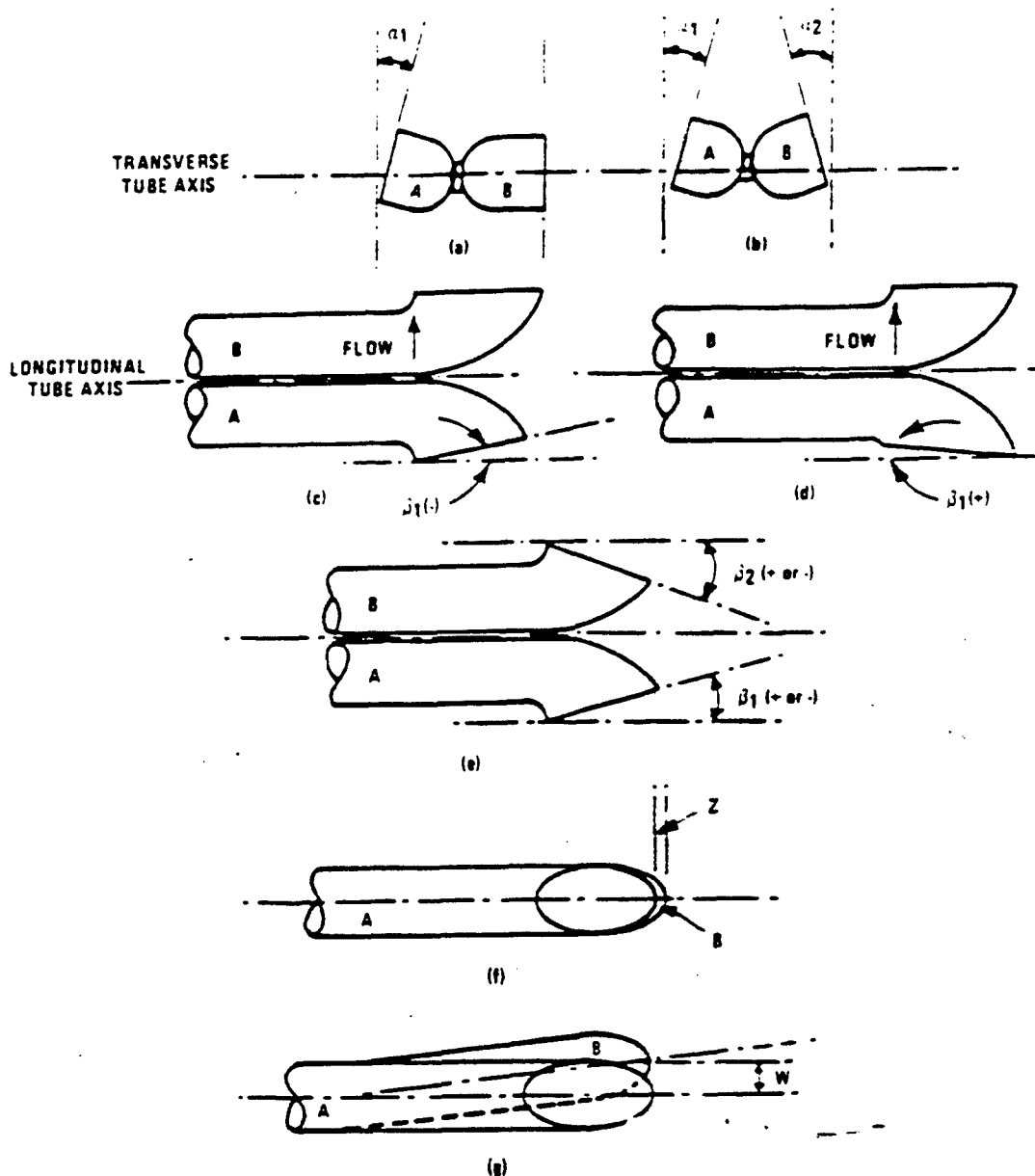


Figure 2-3. Types of face-opening misalignment that can result from field use or improper construction of Type S pitot tubes. These will not affect the baseline value of $C_p(s)$ so long as α_1 and $\alpha_2 \leq 10^\circ$, β_1 and $\beta_2 \leq 5^\circ$, $z \leq 0.32$ cm (1/8 in.) and $w \leq 0.08$ cm (1/32 in.) (citation 11 in Section 6).

A standard pitot tube may be used instead of a Type S, provided that it meets the specifications of Sections 2.7 and 4.2; note, however, that the static and impact pressure holes of standard pitot tubes are susceptible to plugging in particulate-laden gas streams. Therefore, whenever a standard pitot tube is used to perform a traverse, adequate proof must be furnished that the openings of the pitot tube have not plugged up during the traverse period; this can be done by taking a velocity head (Δp) reading at

the final traverse point, cleaning out the impact and static holes of the standard pitot tube by "back-purging" with pressurized air, and then taking another Δp reading. If the Δp readings made before and after the air purge are the same (± 5 percent), the traverse is acceptable. Otherwise, reject the run. Note that if Δp at the final traverse point is unsuitably low, another point may be selected. If "back-purging" at regular intervals is part of the procedure, then comparative Δp readings shall be

taken, as above, for the last two back purges at which suitably high Δp readings are observed.

2.2 Differential Pressure Gauge. An inclined manometer or equivalent device is used. Most sampling trains are equipped with a 10-in. (water column) inclined-vertical manometer, having 0.01-in. H₂O divisions on the 0-to 1-in. inclined scale, and 0.1-in. H₂O divisions on the 1- to 10-in. vertical scale. This type of manometer (or other gauge of equivalent sensitivity) is satisfactory for the measurement of Δp values as low as 1.3 mm (0.05 in.) H₂O. However, a differential pressure gauge of greater sensitivity shall be used (subject to the approval of the Administrator), if any of the following is found to be true: (1) the arithmetic average of all Δp readings at the traverse points in the stack is less than 1.3 mm (0.05 in.) H₂O; (2) for traverses of 12 or more points, more than 10 percent of the individual Δp readings are below 1.3 mm (0.05 in.) H₂O; (3) for traverses of fewer than 12 points, more than one Δp reading is below 1.3 mm (0.05 in.) H₂O. Citation 18 in Section 6 describes commercially available instrumentation for the measurement of low-range gas velocities.

As an alternative to criteria (1) through (3) above, the following calculation may be performed to determine the necessity of using a more sensitive differential pressure gauge:

$$T = \frac{\sum_{i=1}^n \sqrt{\Delta p_i + K}}{\sum_{i=1}^n \sqrt{\Delta p_i}}$$

where:

Δp = Individual velocity head reading at a traverse point, mm H₂O (in. H₂O).

n = Total number of traverse points.

K = 0.13 mm H₂O when metric units are used and 0.005 in. H₂O when English units are used.

If T is greater than 1.05, the velocity head data are unacceptable and a more sensitive differential pressure gauge must be used.

Note: If differential pressure gauges other than inclined manometers are used (e.g., magnetic gauges), their calibration must be checked after each test series. To check

the calibration of a differential pressure gauge, compare Δp readings of the gauge with those of a gauge-oil manometer at a minimum of three points, approximately representing the range of Δp values in the stack. If, at each point, the values of Δp as read by the differential pressure gauge and gauge-oil manometer agree to within 5 percent, the differential pressure gauge shall be considered to be in proper calibration. Otherwise, the test series shall either be voided, or procedures to adjust the measured Δp values and final results shall be used subject to the approval of the Administrator.

2.3 Temperature Gauge. A thermocouple, liquid-filled bulb thermometer, bimetallic thermometer, mercury-in-glass thermometer, or other gauge, capable of measuring temperature to within 1.5 percent of the minimum absolute stack temperature shall be used. The temperature gauge shall be attached to the pitot tube such that the sensor tip does not touch any metal; the gauge shall be in an interference-free arrangement with respect to the pitot tube face openings (see Figure 2-1 and also Figure 2-7 in Section 4). Alternate positions may be used if the pitot tube-temperature gauge system is calibrated according to the procedure of Section 4. Provided that a difference of not more than 1 percent in the average velocity measurement is introduced, the temperature gauge need not be attached to the pitot tube; this alternative is subject to the approval of the Administrator.

2.4 Pressure Probe and Gauge. A piezometer tube and mercury- or water-filled U-tube manometer capable of measuring stack pressure to within 2.5 mm (0.1 in.) Hg is used. The static tap of a standard type pitot tube or one leg of a Type S pitot tube with the face opening planes positioned parallel to the gas flow may also be used as the pressure probe.

2.5 Barometer. A mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 2.5 mm Hg (0.1 in. Hg) may be used. In many cases, the barometric reading may be obtained from a nearby national weather service station, in which case the station value (which is the absolute barometric pressure) shall be requested and an adjustment for elevation differences between the weather station and the sampling point shall be applied at a rate of minus 2.5 mm (0.1 in.) Hg per 30-meter (100 foot) elevation increase or vice-versa for elevation decrease.

2.6 Gas Density Determination Equipment. Method 3 equipment, if needed (see Section 3.6), to determine the stack gas dry molecular weight, and Reference Method 4 or Method 5 equipment for moisture content determination; other methods may be used subject to approval of the Administrator.

2.7 Calibration Pitot Tube. When calibration of the Type S pitot tube is necessary (see Section 4), a standard pitot tube is used as a reference. The standard pitot tube shall, preferably, have a known coefficient, obtained either (1) directly from the National Bureau of Standards, Route 270, Quince Orchard Road, Gaithersburg, Maryland, or (2) by calibration against another standard pitot tube with an NBS-traceable coefficient. Alternatively, a standard pitot tube designed according to the criteria given in 2.7.1 through 2.7.5 below and illustrated in Figure 2-4 (see also Citations 7, 8, and 17 in Section 6) may be used. Pitot tubes designed according to these specifications will have baseline coefficients of about 0.99 ± 0.01 .

2.7.1 Hemispherical (shown in Figure 2-4), ellipsoidal, or conical tip.

2.7.2 A minimum of six diameters straight run (based upon D , the external diameter of the tube) between the tip and the static pressure holes.

2.7.3 A minimum of eight diameters straight run between the static pressure holes and the centerline of the external tube, following the 90 degree bend.

2.7.4 Static pressure holes of equal size (approximately $0.1 D$), equally spaced in a piezometer ring configuration.

2.7.5 Ninety degree bend, with curved or mitered junction.

2.8 Differential Pressure Gauge for Type S Pitot Tube Calibration. An inclined manometer or equivalent is used. If the single-velocity calibration technique is employed (see Section 4.1.2.3), the calibration differential pressure gauge shall be readable to the nearest 0.13 mm H₂O (0.005 in. H₂O). For multiveLOCITY calibrations, the gauge shall be readable to the nearest 0.13 mm H₂O (0.005 in. H₂O) for Δp values between 1.3 and 25 mm H₂O (0.05 and 1.0 in. H₂O), and to the nearest 1.3 mm H₂O (0.05 in. H₂O) for Δp values above 25 mm H₂O (1.0 in. H₂O). A special, more sensitive gauge will be required to read Δp values below 1.3 mm H₂O (0.05 in. H₂O) (see Citation 18 in Section 6).

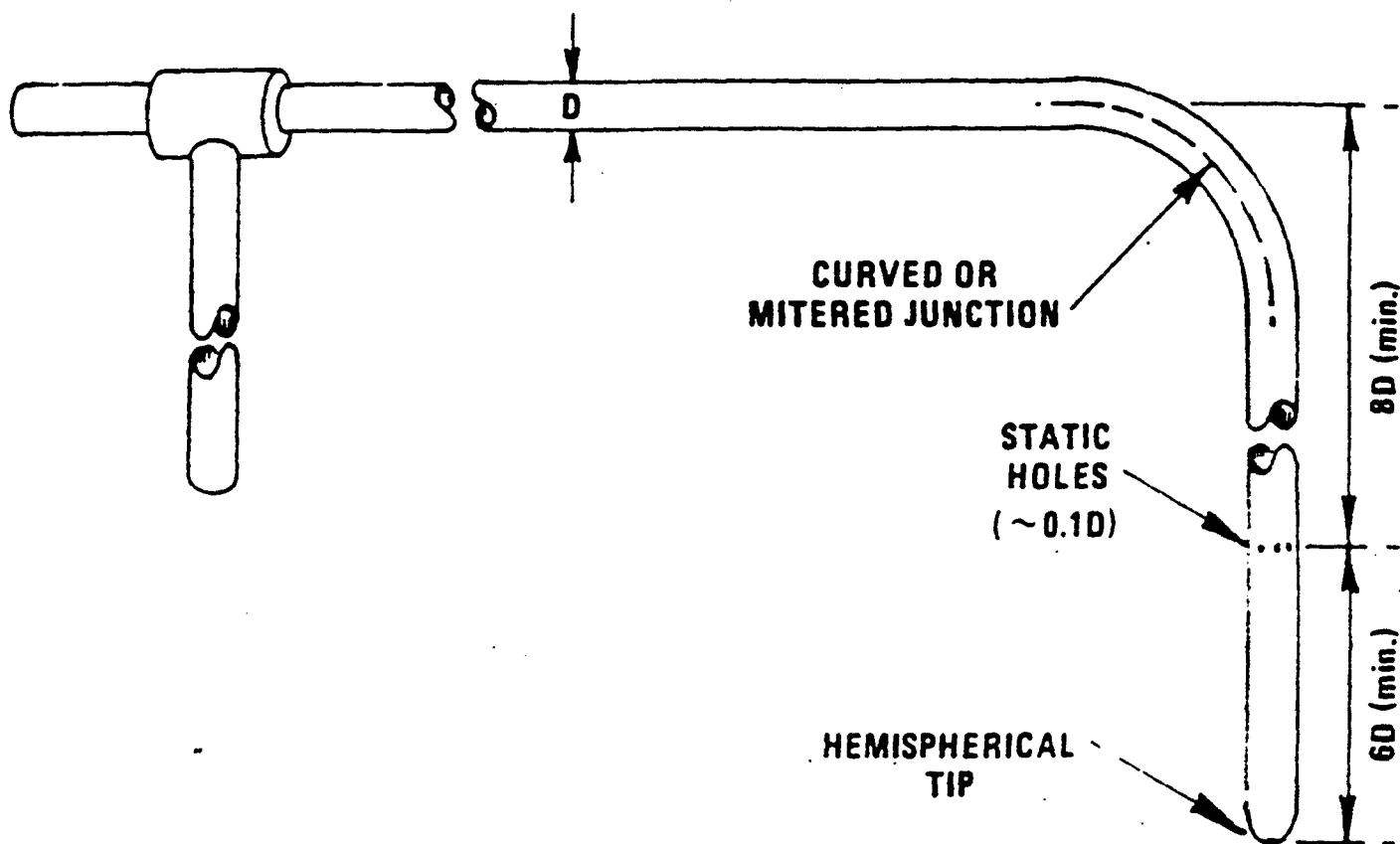


Figure 2-4. Standard pitot tube design specifications.

3. Procedure

3.1 Set up the apparatus as shown in Figure 2-1. Capillary tubing or surge tanks installed between the manometer and pitot tube may be used to dampen Δp fluctuations. It is recommended, but not required, that a pretest leak-check be conducted, as follows: (1) blow through the pitot impact opening until at least 7.6 cm (3 in.) H_2O velocity pressure registers on the manometer; then, close off the impact opening. The pressure shall remain stable for at least 15 seconds; (2) do the same for the static pressure side, except using suction to obtain the minimum of 7.6 cm (3 in.) H_2O . Other leak-check procedures, subject to the approval of the Administrator may be used.

3.2 Level and zero the manometer. Because the manometer level and zero may

drift due to vibrations and temperature changes, make periodic checks during the traverse. Record all necessary data as shown in the example data sheet (Figure 2-5).

3.3 Measure the velocity head and temperature at the traverse points specified by Method 1. Ensure that the proper differential pressure gauge is being used for the range of Δp values encountered (see Section 2.2). If it is necessary to change to a more sensitive gauge, do so, and remeasure the Δp and temperature readings at each traverse point. Conduct a post-test leak-check (mandatory), as described in Section 3.1 above, to validate the traverse run.

3.4 Measure the static pressure in the stack. One reading is usually adequate.

3.5 Determine the atmospheric pressure.

**SCHEMATIC OF STACK
CROSS SECTION**

[illegible]

Figure 2-5. Velocity traverse data.

3.6 Determine the stack gas dry molecular weight. For combustion processes or processes that emit essentially CO₂, O₂, CO, and N₂, use Method 3. For processes emitting essentially air, an analysis need not be conducted; use a dry molecular weight of 29.0. For other processes, other methods, subject to the approval of the Administrator, must be used.

3.7 Obtain the moisture content from Reference Method 4 (or equivalent) or from Method 5.

3.8 Determine the cross-sectional area of the stack or duct at the sampling location. Whenever possible, physically measure the stack dimensions rather than using blueprints.

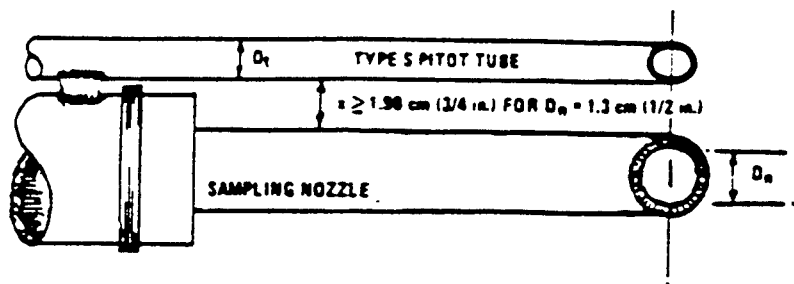
4. Calibration

4.1 Type S Pitot Tube. Before its initial use, carefully examine the Type S pitot tube in top, side, and end views to verify that the face openings of the tube are aligned within the specifications illustrated in Figure 2-2 or 2-3. The pitot tube shall not be used if it fails to meet these alignment specifications.

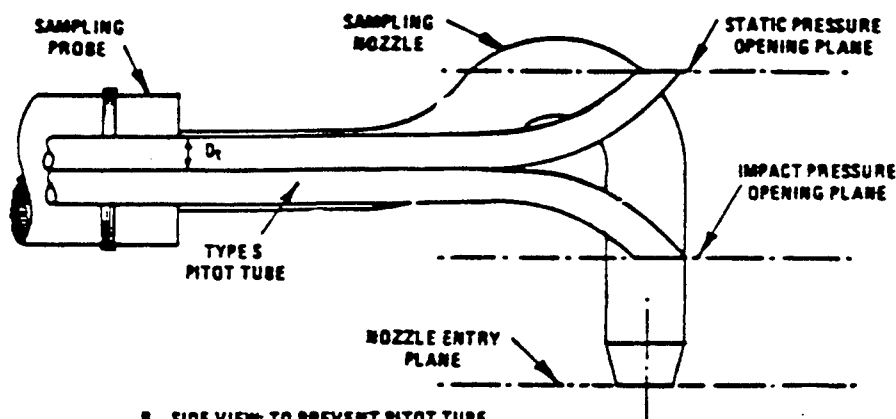
After verifying the face opening alignment, measure and record the following dimensions of the pitot tube: (a) the external tubing diameter (dimension D , Figure 2-2b); and (b) the base-to-opening plane distances (dimensions P and P_1 , Figure 2-2b). If D is between 0.48 and 0.95 cm ($\frac{1}{4}$ and $\frac{3}{8}$ in.) and

If P_1 and P_2 are equal and between 1.05 and 1.50 D, there are two possible options: (1) the pitot tube may be calibrated according to the procedure outlined in Sections 4.1.2 through 4.1.5 below, or (2) a baseline (isolated tube) coefficient value of 0.84 may be assigned to the pitot tube. Note, however, that if the pitot tube is part of an assembly, calibration may still be required, despite knowledge of the baseline coefficient value (see Section 4.1.1).

If D_1 , P_1 , and P_2 are outside the specified limits, the pitot tube must be calibrated outlined in 4.1.2 through 4.1.5 below.



A. BOTTOM VIEW: SHOWING MINIMUM PITOT-NOZZLE SEPARATION.



B. SIDE VIEW: TO PREVENT PITOT TUBE FROM INTERFERING WITH GAS FLOW STREAMLINES APPROACHING THE NOZZLE, THE IMPACT PRESSURE OPENING PLANE OF THE PITOT TUBE SHALL BE EVEN WITH OR ABOVE THE NOZZLE ENTRY PLANE.

Figure 2-6. Proper pitot tube-sampling nozzle configuration to prevent aerodynamic interference: buttonbook-type nozzle; centers of nozzle and pitot opening aligned; D_t between 0.48 and 0.95 cm ($\frac{3}{16}$ and $\frac{3}{8}$ in.).

4.1.1 Type S Pitot Tube Assemblies. During sample and velocity traverses, the isolated Type S pitot tube is not always used; in many instances, the pitot tube is used in combination with other source-sampling components (thermocouple, sampling probe, nozzle) as part of an "assembly." The presence of other sampling components can sometimes affect the baseline value of the Type S pitot tube coefficient (Citation 9 in Section 6); therefore an assigned (or otherwise known) baseline coefficient value may or may not be valid for a given assembly. The baseline and assembly coefficient values will be identical only when the relative placement of the components in the assembly is such that aerodynamic interference effects are eliminated. Figures 2-6 through 2-8 illustrate interference-free component arrangements for Type S pitot tubes having external tubing diameters between 0.48 and 0.95 cm ($\frac{3}{16}$ and $\frac{3}{8}$ in.). Type S pitot tube assemblies that fail to meet any or all of the specifications of Figures 2-6 through 2-8 shall be calibrated according to the procedure outlined in Sections 4.1.2 through 4.1.5 below, and prior to calibration, the values of the intercomponent spacings (pitot-nozzle, pitot-thermocouple, pitot-probe sheath) shall be measured and recorded.

NOTE: Do not use any Type S pitot tube assembly which is constructed such that the impact pressure opening plane of the pitot tube is below the entry plane of the nozzle (see Figure 2-6b).

4.1.2 Calibration Setup. If the Type S pitot tube is to be calibrated, one leg of the tube shall be permanently marked A, and the other, B. Calibration shall be done in a flow system having the following essential design features:

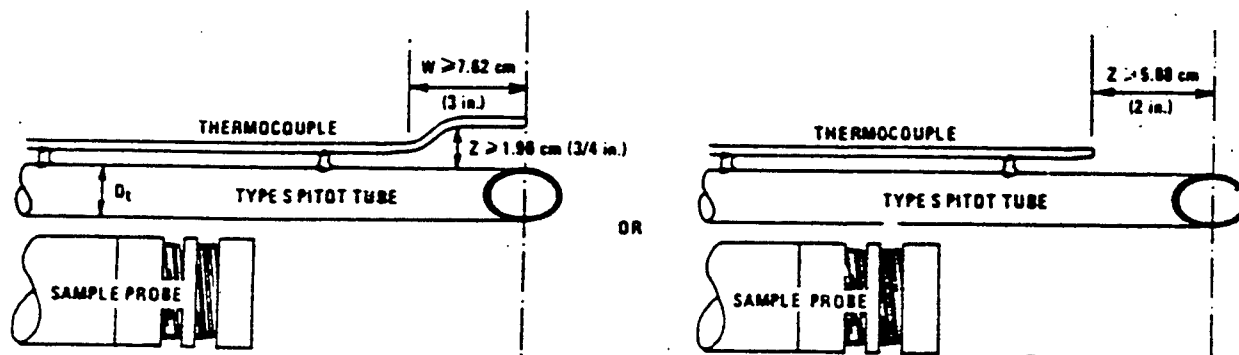


Figure 2-7. Proper thermocouple placement to prevent interference; D_t between 0.48 and 0.95 cm ($\frac{3}{16}$ and $\frac{3}{8}$ in.).

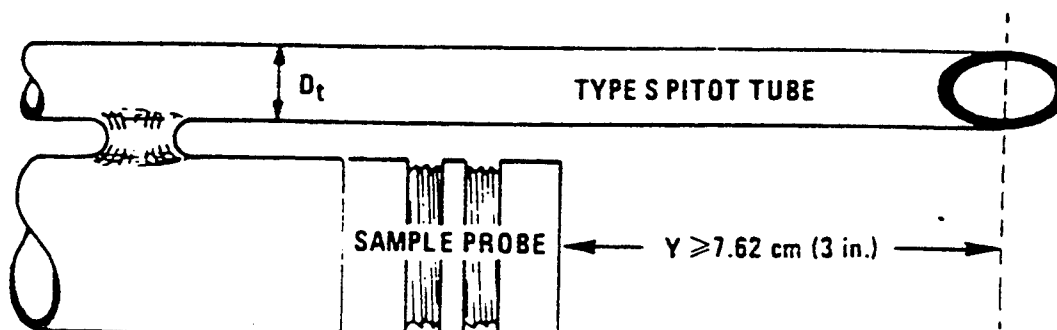


Figure 2-8. Minimum pitot-sample probe separation needed to prevent interference; D_t between 0.48 and 0.95 cm ($\frac{3}{16}$ and $\frac{3}{8}$ in.).

4.1.2.1 The flowing gas stream must be confined to a duct of definite cross-sectional area, either circular or rectangular. For circular cross-sections, the minimum duct diameter shall be 30.5 cm (12 in.); for rectangular cross-sections, the width (shorter side) shall be at least 25.4 cm (10 in.).

4.1.2.2 The cross-sectional area of the calibration duct must be constant over a distance of 10 or more duct diameters. For a rectangular cross-section, use an equivalent diameter, calculated from the following equation, to determine the number of duct diameters:

$$D = \frac{2LW}{(L+W)}$$

Equation 2-1

where:

D = Equivalent diameter

L = Length

W = Width

To ensure the presence of stable, fully developed flow patterns at the calibration site, or "test section," the site must be located at least eight diameters downstream and two diameters upstream from the nearest disturbances.

NOTE: The eight- and two-diameter criteria are not absolute; other test section locations may be used (subject to approval of the Administrator), provided that the flow at the test site is stable and demonstrably parallel to the duct axis.

4.1.2.3 The flow system shall have the capacity to generate a test-section velocity around 915 m/min (3,000 ft/min). This velocity must be constant with time to guarantee steady flow during calibration. Note that Type S pitot tube coefficients obtained by single-velocity calibration at 915 m/min (3,000 ft/min) will generally be valid to within ± 3 percent for the measurement of velocities above 305 m/min (1,000 ft/min) and to within ± 5 to 6 percent for the measurement of velocities between 180 and 305 m/min (600 and 1,000 ft/min). If a more precise correlation between C_p and velocity is desired, the flow system shall have the capacity to generate at least four distinct, time-invariant test-section velocities covering the velocity range from 180 to 1,525 m/min (600 to 5,000 ft/min), and calibration data shall be taken at regular velocity intervals over this range (see Citations 9 and 14 in Section 6 for details).

4.1.2.4 Two entry ports, one each for the standard and Type S pitot tubes, shall be cut in the test section; the standard pitot entry port shall be located slightly downstream of the Type S port, so that the standard and Type S impact openings will lie in the same cross-sectional plane during calibration. To facilitate alignment of the pitot tubes during calibration, it is advisable that the test section be constructed of plexiglas or some other transparent material.

4.1.3 Calibration Procedure. Note that this procedure is a general one and must not be used without first referring to the special considerations presented in Section 4.1.5. Note also that this procedure applies only to single-velocity calibration. To obtain calibration data for the A and B sides of the Type S pitot tube, proceed as follows:

4.1.3.1 Make sure that the manometer is properly filled and that the oil is free from contamination and is of the proper density. Inspect and leak-check all pitot lines; repair or replace if necessary.

PITOT TUBE IDENTIFICATION NUMBER: _____ DATE _____

CALIBRATED BY: _____

"A" SIDE CALIBRATION				
RUN NO.	ΔP_{std} cm H ₂ O (in. H ₂ O)	$\Delta P(s)$ cm H ₂ O (in. H ₂ O)	$C_p(s)$	DEVIATION $C_{p(s)} - \bar{C}_p(A)$
1				
2				
3				
			\bar{C}_p (SIDE A)	

"B" SIDE CALIBRATION				
RUN NO.	ΔP_{std} cm H ₂ O (in. H ₂ O)	$\Delta P(s)$ cm H ₂ O (in. H ₂ O)	$C_p(s)$	DEVIATION $C_{p(s)} - \bar{C}_p(B)$
1				
2				
3				
			\bar{C}_p (SIDE B)	

$$\text{AVERAGE DEVIATION} = \sigma(A \text{ OR } B) = \frac{\sum_{i=1}^3 |C_{p(i)} - \bar{C}_p(A \text{ OR } B)|}{3} \leftarrow \text{MUST BE } < 0.01$$

$$|\bar{C}_p(\text{SIDE A}) - \bar{C}_p(\text{SIDE B})| \leftarrow \text{MUST BE } < 0.01$$

Figure 2-9. Pitot tube calibration data.

4.1.3.2 Level and zero the manometer. Turn on the fan and allow the flow to stabilize. Seal the Type S entry port.

4.1.3.3 Ensure that the manometer is level and zeroed. Position the standard pitot tube at the calibration point (determined as outlined in Section 4.1.5.1), and align the tube so that its tip is pointed directly into the flow. Particular care should be taken in aligning the tube to avoid yaw and pitch angles. Make sure that the entry port surrounding the tube is properly sealed.

4.1.3.4 Read ΔP_{std} and record its value in a data table similar to the one shown in Figure 2-9. Remove the standard pitot tube from the duct and disconnect it from the manometer. Seal the standard entry port.

4.1.3.5 Connect the Type S pitot tube to the manometer. Open the Type S entry port. Check the manometer level and zero. Insert and align the Type S pitot tube so that its A side impact opening is at the same

point as was the standard pitot tube and is pointed directly into the flow. Make sure that the entry port surrounding the tube is properly sealed.

4.1.3.6 Read ΔP_s and enter its value in the data table. Remove the Type S pitot tube from the duct and disconnect it from the manometer.

4.1.3.7 Repeat steps 4.1.3.3 through 4.1.3.6 above until three pairs of ΔP readings have been obtained.

4.1.3.8 Repeat steps 4.1.3.3 through 4.1.3.7 above for the B side of the Type S pitot tube.

4.1.3.9 Perform calculations, as described in Section 4.1.4 below.

4.1.4 Calculations.

4.1.4.1 For each of the six pairs of ΔP readings (i.e., three from side A and three from side B) obtained in Section 4.1.3 above, calculate the value of the Type S pitot tube coefficient as follows:

$$C_{p,s} = C_{p,standard} \sqrt{\frac{\Delta p_{standard}}{\Delta p_s}}$$

Equation 2-2

here:

$C_{p,s}$ = Type S pitot tube coefficient

$C_{p,standard}$ = Standard pitot tube coefficient: use 0.99 if the coefficient is unknown and the tube is designed according to the criteria of Sections 2.7.1 to 2.7.5 of this method.

$\Delta p_{standard}$ = Velocity head measured by the standard pitot tube, cm H₂O (in. H₂O)

Δp_s = Velocity head measured by the Type S pitot tube, cm H₂O (in. H₂O)

4.1.4.2 Calculate \bar{C}_p (side A), the mean A-side coefficient, and \bar{C}_p (side B), the mean B-side coefficient; calculate the difference between these two average values.

4.1.4.3 Calculate the deviation of each of the three A-side values of $\bar{C}_{p,s}$ from \bar{C}_p (side A), and the deviation of each B-side value of $\bar{C}_{p,s}$ from \bar{C}_p (side B). Use the following equation:

$$\text{Deviation} = C_{p,s} - \bar{C}_p (\text{A or B})$$

Equation 2-3

4.1.4.4 Calculate σ , the average deviation from the mean, for both the A and B sides of the pitot tube. Use the following equation:

$$\sigma \text{ (side A or B)} = \frac{\sum_{i=1}^3 |C_{p,s,i} - \bar{C}_p (\text{A or B})|}{3}$$

Equation 2-4

4.1.4.5 Use the Type S pitot tube only if the values of σ (side A) and σ (side B) are less than or equal to 0.01 and if the absolute value of the difference between \bar{C}_p (A) and \bar{C}_p (B) is 0.01 or less.

4.1.5 Special considerations.

4.1.5.1 Selection of calibration point.

4.1.5.1.1 When an isolated Type S pitot tube is calibrated, select a calibration point at or near the center of the duct, and follow the procedures outlined in Sections 4.1.3 and 4.1.4 above. The Type S pitot coefficients so obtained, i.e., \bar{C}_p (side A) and \bar{C}_p (side B), will be valid, so long as either: (1) the isolated pitot tube is used; or (2) the pitot tube is used with other components (nozzle, thermocouple, sample probe) in an arrangement that is free from aerodynamic interference effects (see Figures 2-6 through 2-8).

4.1.5.1.2 For Type S pitot tube-thermocouple combinations (without sample probe), select a calibration point at or near the center of the duct, and follow the procedures outlined in Sections 4.1.3 and 4.1.4 above. The coefficients so obtained will be valid so long as the pitot tube-thermocouple combination is used by itself or with other components in an interference-free arrangement (Figures 2-6, and 2-8).

4.1.5.1.3 For assemblies with sample probes, the calibration point should be located at or near the center of the duct; however, insertion of a probe sheath into a small duct may cause significant cross-sectional area blockage and yield incorrect coefficient values (Citation 9 in Section 6). Therefore, to minimize the blockage effect, the calibration point may be a few inches

off-center if necessary. The actual blockage effect will be negligible when the theoretical blockage, as determined by a projected-area model of the probe sheath, is 2 percent or less of the duct cross-sectional area for assemblies without external sheaths (Figure 2-10a), and 3 percent or less for assemblies with external sheaths (Figure 2-10b).

4.1.5.2 For those probe assemblies in which pitot tube-nozzle interference is a factor (i.e., those in which the pitot-nozzle separation distance fails to meet the specification illustrated in Figure 2-8a), the value of $C_{p,s}$ depends upon the amount of free-space between the tube and nozzle, and therefore is a function of nozzle size. In these instances, separate calibrations shall be performed with each of the commonly used nozzle sizes in place. Note that the single-velocity calibration technique is acceptable for this purpose, even though the larger nozzle sizes (>0.635 cm or 1/4 in.) are not ordinarily used for isokinetic sampling at velocities around 915 m/min (3,000 ft/min), which is the calibration velocity; note also that it is not necessary to draw an isokinetic sample during calibration (see Citation 19 in Section 6).

4.1.5.3 For a probe assembly constructed such that its pitot tube is always used in the same orientation, only one side of the pitot tube need be calibrated (the side which will face the flow). The pitot tube must still meet the alignment specifications of Figure 2-2 or 2-3, however, and must have an average deviation (σ) value of 0.01 or less (see Section 4.1.4.4).

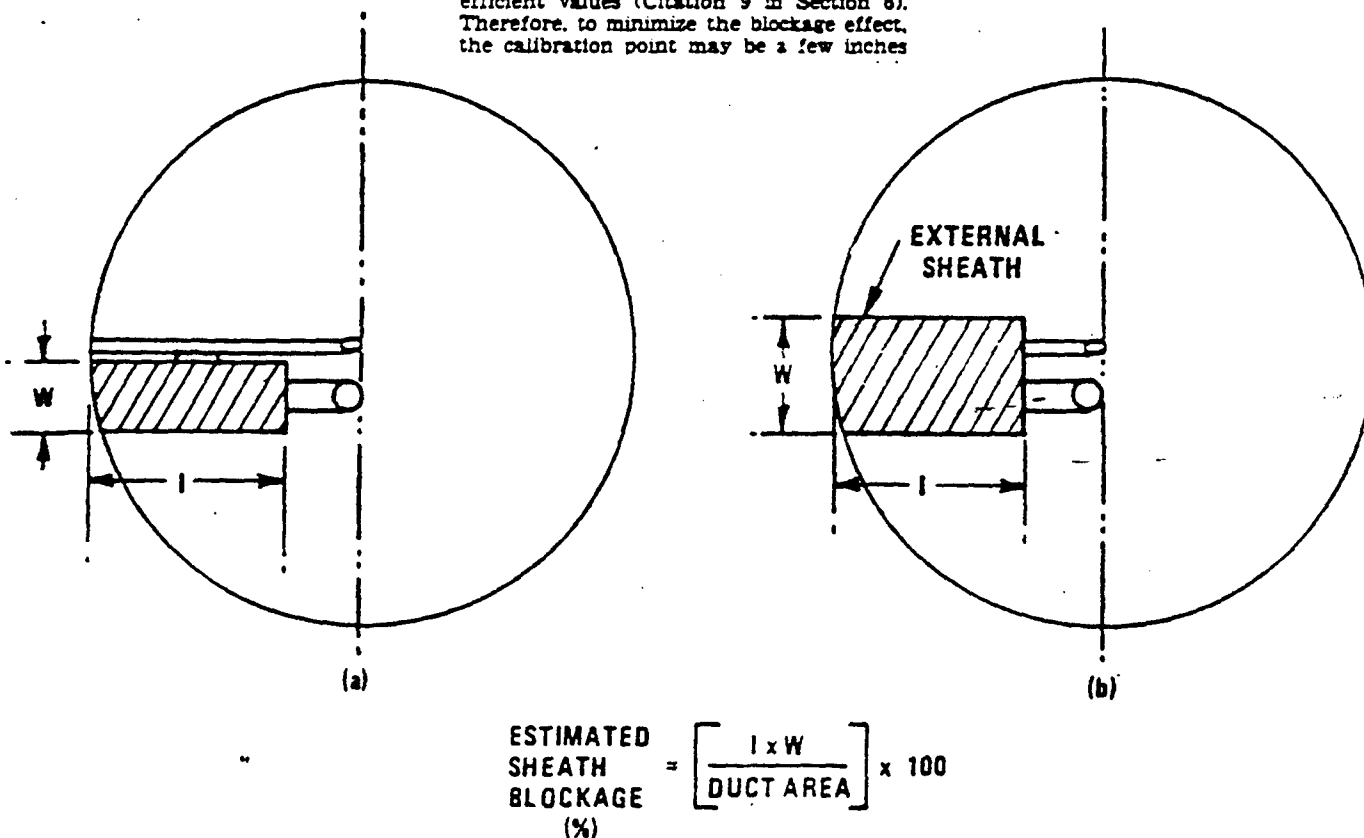


Figure 2-10. Projected-area models for typical pitot tube assemblies.

Figure 2-10. Projected-area models for typical pitot tube assemblies.

4.1.6 Field Use and Recalibration.

4.1.6.1 Field Use.

4.1.6.1.1 When a Type S pitot tube (isolated tube or assembly) is used in the field, the appropriate coefficient value (whether assigned or obtained by calibration) shall be used to perform velocity calculations. For calibrated Type S pitot tubes, the A side coefficient shall be used when the A side of the tube faces the flow, and the B side coefficient shall be used when the B side faces the flow; alternatively, the arithmetic average of the A and B side coefficient values may be used, irrespective of which side faces the flow.

4.1.6.1.2 When a probe assembly is used to sample a small duct (12 to 36 in. in diameter), the probe sheath sometimes blocks a significant part of the duct cross-section, causing a reduction in the effective value of $C_{p_{avg}}$. Consult Citation 9 in Section 6 for details. Conventional pitot-sampling probe assemblies are not recommended for use in ducts having inside diameters smaller than 12 inches (Citation 16 in Section 6).

4.1.6.2 Recalibration.

4.1.6.2.1 Isolated Pitot Tubes. After each field use, the pitot tube shall be carefully reexamined in top, side, and end views. If the pitot face openings are still aligned within the specifications illustrated in Figure 2-2 or 2-3, it can be assumed that the baseline coefficient of the pitot tube has not changed. If, however, the tube has been damaged to the extent that it no longer meets the specifications of Figure 2-2 or 2-3, the damage shall either be repaired to restore proper alignment of the face openings or the tube shall be discarded.

4.1.6.2.2 Pitot Tube Assemblies. After each field use, check the face opening alignment of the pitot tube, as in Section 4.1.6.2.1; also, remeasure the intercomponent spacings of the assembly. If the intercomponent spacings have not changed and the face opening alignment is acceptable, it can be assumed that the coefficient of the assembly has not changed. If the face opening alignment is no longer within the specifications of Figures 2-2 or 2-3, either repair the damage or replace the pitot tube (calibrating the new assembly, if necessary). If the intercomponent spacings have changed, restore the original spacings or recalibrate the assembly.

4.2 Standard pitot tube (if applicable). If a standard pitot tube is used for the velocity traverse, the tube shall be constructed according to the criteria of Section 2.7 and shall be assigned a baseline coefficient value of 0.99. If the standard pitot tube is used as part of an assembly, the tube shall be in an interference-free arrangement (subject to the approval of the Administrator).

4.3 Temperature Gauges. After each field use, calibrate dial thermometers, liquid-filled bulb thermometers, thermocouple-potentiometer systems, and other gauges at a temperature within 10 percent of the average absolute stack temperature. For temperatures up to 405° C (761° F), use an ASTM mercury-in-glass reference thermometer, or equivalent, as a reference; alternatively, either a reference thermocouple and potentiometer (calibrated by NBS) or thermometric fixed points, e.g., ice bath and boiling water (corrected for barometric pressure) may be used. For temperatures above 405° C (761° F), use an NBS-calibrated reference thermocouple-potentiometer system or an alternate reference, subject to the approval of the Administrator.

If, during calibration, the absolute temperatures measured with the gauge being calibrated and the reference gauge agree within 1.5 percent, the temperature data taken in the field shall be considered valid. Otherwise, the pollutant emission test shall either be considered invalid or adjustments (if appropriate) of the test results shall be made, subject to the approval of the Administrator.

4.4 Barometer. Calibrate the barometer used against a mercury barometer.

5. Calculations

Carry out calculations, retaining at least one extra decimal figure beyond that of the acquired data. Round off figures after final calculation.

5.1 Nomenclature.

A = Cross-sectional area of stack, m^2 (ft^2).

B_w = Water vapor in the gas stream (from Method 5 or Reference Method 4), proportion by volume.

C_p = Pitot tube coefficient, dimensionless.

K_p = Pitot tube constant.

$$34.97 \frac{m}{sec} \left[\frac{(g/g\text{-mole})(mm\ Hg)}{(^{\circ}K)(mm\ H_2O)} \right]^{1/2}$$

for the metric system and

$$85.49 \frac{ft}{sec} \left[\frac{(lb\ lb\text{-mole})(in.\ Hg)}{(^{\circ}R)(in.\ H_2O)} \right]^{1/2}$$

for the English system.

M_d = Molecular weight of stack gas, dry basis (see Section 3.6) $g/g\text{-mole}$ ($lb/lb\text{-mole}$).

M_w = Molecular weight of stack gas, wet basis, $g/g\text{-mole}$ ($lb/lb\text{-mole}$).

$= M_d(1 - B_w) + 18.0 B_w$

Equation 2-5

P_{atm} = Barometric pressure at measurement site, mm Hg (in. Hg).

P_s = Stack static pressure, mm Hg (in. Hg).

P_t = Absolute stack gas pressure, mm Hg (in. Hg).

$= P_{atm} + P_s$

Equation 2-6

P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).

Q_d = Dry volumetric stack gas flow rate corrected to standard conditions, $dscm/hr$ ($dscf/hr$).

t = Stack temperature, °C (°F).

T = Absolute stack temperature, °K (°R).

$= 273 + t$ for metric

Equation 2-7

$= 460 + t$ for English

Equation 2-8

T_{std} = Standard absolute temperature, 293 °K (528° R)

v = Average stack gas velocity, m/sec (ft/sec).

Δh = Velocity head of stack gas, mm H_2O (in. H_2O).

3,600 = Conversion factor, sec/hr .

18.0 = Molecular weight of water, $g/g\text{-mole}$ ($lb/lb\text{-mole}$).

5.2 Average stack gas velocity.

$$v = K_p C_p (\sqrt{\Delta h}) \dots \sqrt{\frac{T_{std}}{P_{std} M_d}}$$

Equation 2-9

5.3 Average stack gas dry volumetric flow rate.

$$Q_d = 3,600(1 - B_w)vA \left(\frac{T_{std}}{T_{avg}} \right) \left(\frac{P_s}{P_{std}} \right)$$

Equation 2-10

To convert Q_d from $dscm/hr$ ($dscf/hr$) to $dscm/min$ ($dscf/min$), divide Q_d by 60.

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METHOD 3

Gas Analysis for Carbon Dioxide,
Oxygen, Excess Air, and
Dry Molecular Weight

METHOD 3—GAS ANALYSIS FOR CARBON DIOXIDE, OXYGEN, EXCESS AIR, AND DRY MOLECULAR WEIGHT

1. Principle and Applicability

1.1 Principle. A gas sample is extracted from a stack, by one of the following methods: (1) single-point, grab sampling; (2) single-point, integrated sampling; or (3) multi-point, integrated sampling. The gas sample is analyzed for percent carbon dioxide (CO_2), percent oxygen (O_2), and, if necessary, percent carbon monoxide (CO). If a dry molecular weight determination is to be made, either an Orsat or a Fyrite¹ analyzer may be used for the analysis; for excess air or emission rate correction factor determination, an Orsat analyzer must be used.

1.2 Applicability. This method is applicable for determining CO_2 and O_2 concentrations, excess air, and dry molecular weight of a sample from a gas stream of a fossil-fuel combustion process. The method may also be applicable to other processes where it has been determined that compounds other than CO_2 , O_2 , CO , and nitrogen (N_2) are not present in concentrations sufficient to affect the results.

Other methods, as well as modifications to the procedure described herein, are also applicable for some or all of the above determinations. Examples of specific methods and modifications include: (1) a multi-point sampling method using an Orsat analyzer to analyze individual grab samples obtained at each point; (2) a method using CO_2 or O_2 and stoichiometric calculations to determine dry molecular weight and excess air; (3) assigning a value of 30.0 for dry molecular weight, in lieu of actual measurements, for processes burning natural gas, coal, or oil. These methods and modifications may be used, but are subject to the approval of the Administrator, U.S. Environmental Protection Agency.

2. Apparatus

As an alternative to the sampling apparatus and systems described herein, other sampling systems (e.g., liquid displacement) may be used provided such systems are capable of obtaining a representative sample and maintaining a constant sampling rate, and are otherwise capable of yielding acceptable results. Use of such systems is subject to the approval of the Administrator.

2.1 Grab Sampling (Figure 3-1).

2.1.1 Probe. The probe should be made of stainless steel or borosilicate glass tubing and should be equipped with an in-stack or out-stack filter to remove particulate matter (a plug of glass wool is satisfactory for this purpose). Any other materials inert to O_2 , CO_2 , CO , and N_2 and resistant to temperature at sampling conditions may be used for the probe; examples of such material are aluminum, copper, quartz glass and Teflon.

2.1.2 Pump. A one-way squeeze bulb, or equivalent, is used to transport the gas sample to the analyzer.

2.2 Integrated Sampling (Figure 3-2).

2.2.1 Probe. A probe such as that described in Section 2.1.1 is suitable.

2.2.2 Condenser. An air-cooled or water-cooled condenser, or other condenser that will not remove O_2 , CO_2 , CO , and N_2 , may be used to remove excess moisture which would interfere with the operation of the pump and flow meter.

2.2.3 Valve. A needle valve is used to adjust sample gas flow rate.

2.2.4 Pump. A leak-free, diaphragm-type pump, or equivalent, is used to transport sample gas to the flexible bag. Install a small surge tank between the pump and rate meter to eliminate the pulsation effect of the diaphragm pump on the rotameter.

2.2.5 Rate Meter. The rotameter, or equivalent rate meter, used should be capable of measuring flow rate to within ± 2 percent of the selected flow rate. A flow rate range of 500 to 1000 cm^3/min is suggested.

2.2.6 Flexible Bag. Any leak-free plastic (e.g., Tedlar, Mylar, Teflon) or plastic-coated aluminum (e.g., aluminized Mylar) bag, or equivalent, having a capacity consistent with the selected flow rate and time

length of the test run, may be used. A capacity in the range of 55 to 90 liters is suggested.

To leak-check the bag, connect it to a water manometer and pressurize the bag to 5 to 10 cm H_2O (2 to 4 in. H_2O). Allow to stand for 10 minutes. Any displacement in the water manometer indicates a leak. An alternative leak-check method is to pressurize the bag to 5 to 10 cm H_2O (2 to 4 in. H_2O) and allow to stand overnight. A deflated bag indicates a leak.

2.2.7 Pressure Gauge. A water-filled U-tube manometer, or equivalent, of about 30 cm (12 in.) is used for the flexible bag leak-check.

2.2.8 Vacuum Gauge. A mercury manometer, or equivalent, of at least 760 mm Hg (30 in. Hg) is used for the sampling train leak-check.

2.3 Analysis. For Orsat and Fyrite analyzer maintenance and operation procedures, follow the instructions recommended by the manufacturer, unless otherwise specified herein.

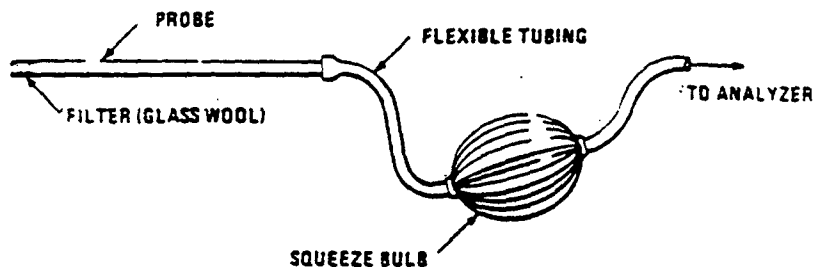


Figure 3-1. Grab-sampling train.

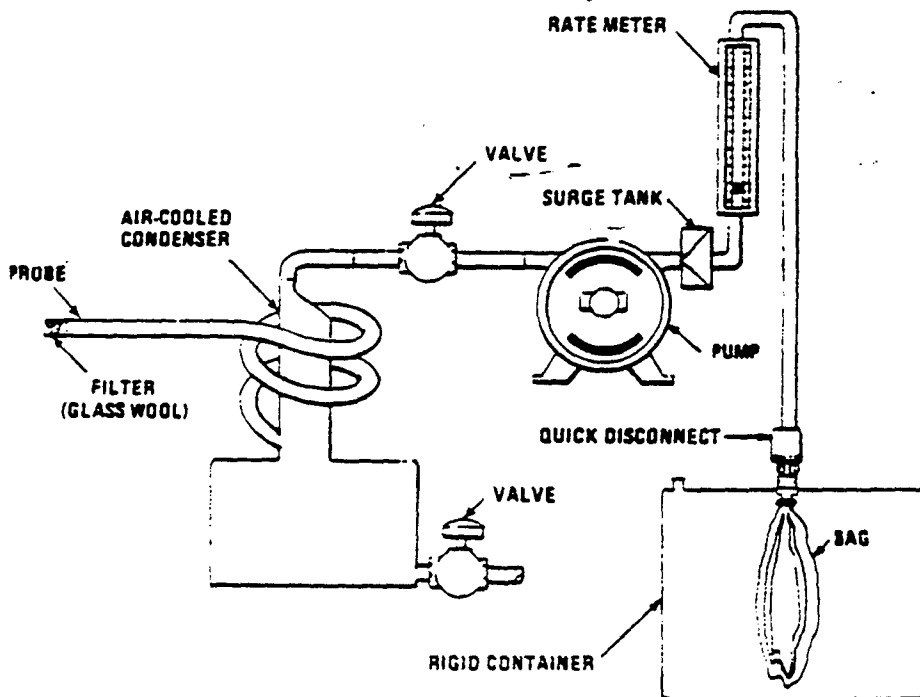


Figure 3-2. Integrated gas-sampling train.

¹ Mention of trade names or specific products does not constitute endorsement by the Environmental Protection Agency.

2.3.2 Emission Rate Correction Factor or Excess Air Determination. An Orsat analyzer must be used. For low CO₂ (less than 4.0 percent) or high O₂ (greater than 15.0 percent) concentrations, the measuring burette of the Orsat must have at least 0.1 percent subdivisions.

Any of the three sampling and analytical procedures described below may be used for determining the dry molecular weight.

3.1.1 The sampling point in the duct shall either be at the centroid of the cross section or at a point no closer to the walls than 1.00 m (3.3 ft), unless otherwise specified by the Administrator.

3.1.2 Set up the equipment as shown in Figure 3-1, making sure all connections ahead of the analyzer are tight and leak-free. If an Orsat analyzer is used, it is recommended that the analyzer be leak-checked by following the procedure in Section 5; however, the leak-check is optional.

3.1.3 Place the probe in the stack, with the tip of the probe positioned at the sampling point; purge the sampling line. Draw a sample into the analyzer and immediately analyze it for percent CO₂ and percent O₂. Determine the percentage of the gas that is N₂ and CO by subtracting the sum of the percent CO₂ and percent O₂ from 100 percent. Calculate the dry molecular weight as indicated in Section 6.3.

3.1.4 Repeat the sampling, analysis, and calculation procedures, until the dry molecular weights of any three grab samples differ from their mean by no more than 0.3 g/g-mole (0.3 lb/lb-mole). Average these three molecular weights, and report the results to the nearest 0.1 g/g-mole (lb/lb-mole).

3.2.1 The sampling point in the duct shall be located as specified in Section 3.1.1.

ment as shown in Figure 3-2. Just prior to sampling, leak-check (optional) the train by placing a vacuum gauge at the condenser inlet, pulling a vacuum of at least 250 mm Hg (10 in. Hg), plugging the outlet at the quick disconnect, and then turning off the pump. The vacuum should remain stable for at least 0.5 minute. Evacuate the flexible bag. Connect the probe and place it in the stack, with the tip of the probe positioned at the sampling point; purge the sampling line. Next, connect the bag and make sure that all connections are tight and leak free.

3.2.3 Sample at a constant rate. The sampling run should be simultaneous with, and for the same total length of time as, the pollutant emission rate determination. Collection of at least 30 liters (1.00 ft³) of sample gas is recommended; however, smaller volumes may be collected, if desired.

3.2.4 Obtain one integrated flue gas sample during each pollutant emission rate determination. Within 8 hours after the sample is taken, analyze it for percent CO, and percent O₂ using either an Orsat analyzer or a Fyrite-type combustion gas analyzer. If an Orsat analyzer is used, it is recommended that the Orsat leak-check described in Section 5 be performed before this determination; however, the check is optional.

Determine the percentage of the gas that is N_2 and CO by subtracting the sum of the percent CO_2 and percent O_2 from 100 percent. Calculate the dry molecular weight as indicated in Section 6.3.

3.2.5 Repeat the analysis and calculation procedures until the individual dry molecular weights for any three analyses differ from their mean by no more than 0.3 g/g-mole (0.3 lb/lb-mole). Average these three molecular weights, and report the results to the nearest 0.1 g-mole (0.1 lb/lb-mole).

3.3.1 Unless otherwise specified by the Administrator, a minimum of eight traverse points shall be used for circular stacks having diameters less than 0.61 m (24 in.), a minimum of nine shall be used for rectangular stacks having equivalent diameters less than 0.61 m (24 in.), and a minimum of twelve traverse points shall be used for all other cases. The traverse points shall be located according to Method 1. The use of fewer points is subject to approval of the Administrator.

3.3.2 Follow the procedures outlined in sections 3.2.2 through 3.2.5, except for the following: traverse all sampling points and sample at each point for an equal length of time. Record sampling data as shown in Figure 3-3.

NOTE: A Pyrite-type combustion gas analyzer is not acceptable for excess air or emission rate correction factor determination, unless approved by the Administrator. If both percent CO₂ and percent O₂ are measured, the analytical results of any of the three procedures given below may also be used for calculating the dry molecular weight.

Each of the three procedures below shall be used only when specified in an applicable subpart of the standards. The use of these procedures for other purposes must have specific prior approval of the Administrator.

4.1.1 The sampling point in the duct shall either be at the centroid of the cross-section or at a point no closer to the walls than 1.00 m (3.3 ft), unless otherwise specified by the Administrator.

4.1.2 Set up the equipment as shown in Figure 3-1, making sure all connections ahead of the analyzer are tight and leak-free. Leak-check the Orsat analyzer according to the procedure described in Section 5. This leak-check is mandatory.

Time	Transverse dist.	Q diam	% dev. ^a
Average.....			

$$\% \text{ Dev.} = (Q - Q_{\text{avg}}) / Q_{\text{avg}} \times 100 \quad (\text{Must be } < |10\%|)$$

4.1.3 Place the probe in the stack, with the tip of the probe positioned at the sampling point; purge the sampling line. Draw a sample into the analyzer. For emission rate correction factor determination, immediately analyze the sample, as outlined in Sections 4.1.4 and 4.1.5, for percent CO, or percent O₂. If excess air is desired, proceed as follows: (1) immediately analyze the sample, as in Sections 4.1.4 and 4.1.5, for percent CO₂, O₂, and CO; (2) determine the percentage of the gas that is N₂ by subtracting the sum of the percent CO₂, percent O₂, and percent CO from 100 percent; and (3) calculate percent excess air as outlined in Section 6.2.

4.1.4 To insure complete absorption of the CO_2 , O_2 , or if applicable, CO , make repeated passes through each absorbing solution until two consecutive readings are the same. Several passes (three or four) should be made between readings. (If constant readings cannot be obtained after three consecutive readings, replace the absorbing solution.)

4.1.5 After the analysis is completed, leak-check (mandatory) the Orsat analyzer once again, as described in Section 5. For the results of the analysis to be valid, the Orsat analyzer must pass this leak test before and after the analysis.

NOTE: Since this single-point, grab sampling and analytical procedure is normally conducted in conjunction with a single-point, grab sampling and analytical procedure for a pollutant, only one analysis is ordinarily conducted. Therefore, great care must be taken to obtain a valid sample and analysis. Although in most cases only CO, or O₂, is required, it is recommended that both CO, and O₂ be measured, and that Section 4.4 be used to validate the analytical data.

4.2.1 The sampling point in the duct shall be located as specified in Section 4.1.1.

4.2.2 Leak-check (mandatory) the flexi-

ble bag as in Section 2.2.6. Set up the equipment as shown in Figure 3-2. Just prior to sampling, leak-check (mandatory) the train by placing a vacuum gauge at the condenser inlet, pulling a vacuum of at least 250 mm Hg (10 in. Hg), plugging the outlet at the quick disconnect, and then turning off the pump. The vacuum shall remain stable for at least 0.5 minute. Evacuate the flexible bag. Connect the probe and place it in the stack with the tip of the probe positioned at the sampling point; purge the sampling line. Next, connect the bag and make sure that all connections are tight and leak free.

4.2.3 Sample at a constant rate, or as specified by the Administrator. The sampling run must be simultaneous with, and for the same total length of time as, the pollutant emission rate determination. Collect at least 30 liters (1.00 ft³) of sample gas. Smaller volumes may be collected, subject to approval of the Administrator.

4.2.4 Obtain one integrated flue gas sample during each pollutant emission rate determination. For emission rate correction factor determination, analyze the sample within 4 hours after it is taken for percent CO, or percent O₂ (as outlined in Sections 4.2.5 through 4.2.7). The Orsat analyzer must be leak-check (see Section 5) before the analysis. If excess air is desired, proceed as follows: (1) within 4 hours after the sample is taken, analyze it (as in Sections 4.2.5 through 4.2.7) for percent CO, O₂, and CO; (2) determine the percentage of the gas that is N₂ by subtracting the sum of the percent CO, percent O₂, and percent CO from 100 percent; (3) calculate percent excess air, as outlined in Section 6.2.

4.2.5 To insure complete absorption of the CO₂, O₂, or if applicable, CO, make repeated passes through each absorbing solution until two consecutive readings are the same. Several passes (three or four) should be made between readings. (If constant readings cannot be obtained after three consecutive readings, replace the absorbing solution.)

4.2.6 Repeat the analysis until the following criteria are met:

4.2.6.1 For percent CO₂, repeat the analytical procedure until the results of any three analyses differ by no more than (a) 0.3 percent by volume when CO₂ is greater than 4.0 percent or (b) 0.2 percent by volume when CO₂ is less than or equal to 4.0 percent. Average the three acceptable values of percent CO₂ and report the results to the nearest 0.1 percent.

4.2.6.2 For percent O₂, repeat the analytical procedure until the results of any three analyses differ by no more than (a) 0.3 percent by volume when O₂ is less than 15.0 percent or (b) 0.2 percent by volume when O₂ is greater than or equal to 15.0 percent. Average the three acceptable values of percent O₂ and report the results to the nearest 0.1 percent.

4.2.6.3 For percent CO, repeat the analytical procedure until the results of any three analyses differ by no more than 0.3 percent. Average the three acceptable values of percent CO and report the results to the nearest 0.1 percent.

4.2.7 After the analysis is completed, leak-check (mandatory) the Orsat analyzer once again, as described in Section 5. For the results of the analysis to be valid, the Orsat analyzer must pass this leak test before an after the analysis.

NOTE: Although in most instances only CO₂ or O₂ is required, it is recommended that both CO₂ and O₂ be measured, and that Section 4.4.1 be used to validate the analytical data.

4.3 Multi-Point, Integrated Sampling and Analytical Procedure.

4.3.1 Both the minimum number of sampling points and the sampling point location shall be as specified in Section 3.3.1 of this method. The use of fewer points than specified is subject to the approval of the Administrator.

4.3.2 Follow the procedures outlined in Sections 4.2.2 through 4.2.7, except for the following: Traverse all sampling points and sample at each point for an equal length of time. Record sampling data as shown in Figure 3-3.

4.4 Quality Control Procedures.

4.4.1 Data Validation When Both CO₂ and O₂ Are Measured. Although in most instances, only CO₂ or O₂ measurement is required, it is recommended that both CO₂ and O₂ be measured to provide a check on the quality of the data. The following quality control procedure is suggested.

NOTE: Since the method for validating the CO₂ and O₂ analyses is based on combustion of organic and fossil fuels and dilution of the gas stream with air, this method does not apply to sources that: (1) remove CO₂ or O₂ through processes other than combustion, (2) add O₂ (e.g., oxygen enrichment) and N₂ in proportions different from that of air, (3) add CO₂ (e.g., cement or lime kilns), or (4) have no fuel factor. F₁ values obtainable (e.g., extremely variable waste mixtures). This method validates the measured proportions of CO₂ and O₂ for the fuel type, but the method does not detect sample dilution resulting from leaks during or after sample collection. The method is applicable

for samples collected downstream of most lime or limestone flue-gas desulfurization units as the CO₂ added or removed from the gas stream is not significant in relation to the total CO₂ concentration. The CO₂ concentrations from other types of scrubbers using only water or basic slurry can be significantly affected and would render the F₁ check minimally useful.

4.4.1.1 Calculate a fuel factor, F₁, using the following equation:

$$F_1 = \frac{20.9 - \%O_2}{\%CO_2}$$

Eq. 3-3

Where:

%O₂ = Percent O₂ by volume (dry basis).

%CO₂ = Percent CO₂ by volume (dry basis).

20.9 = Percent O₂ by volume in ambient air.

If CO is present in quantities measurable by this method, adjust the O₂ and CO₂ values before performing the calculation for F₁ as follows:

$$\%CO_2(\text{adj}) = \%CO_2 - \%CO$$

$$\%O_2(\text{adj}) = \%O_2 - 0.5 \%CO$$

Where: %CO = Percent CO by volume (dry basis).

4.4.1.2 Compare the calculated F₁ factor with the expected F₁ values. The following table may be used in establishing acceptable ranges for the expected F₁ if the fuel being burned is known. When fuels are burned in combination, calculate the combined fuel F₁ and F₁ factors (as defined in Method 19) according to the procedure in Method 19 Section 5.2.3. Then calculate the F₁ factor as follows:

$$F_1 = \frac{0.209 F_1}{F_1}$$

Eq. 3-4

Fuel type	F ₁ range
Coal:	
Anthracite and lignite	1.016-1.130
Bituminous	1.063-1.230
Oil:	
Diesel	1.280-1.413
Residual	1.210-1.370
Gas:	
Natural	1.600-1.836
Propane	1.434-1.586
Butane	1.405-1.553
Wood	1.000-1.120
Wood bark	1.003-1.130

Calculated F₁ values beyond the acceptable ranges shown in this table should be investigated before accepting the test results. For example, the strength of the solutions in the gas analyzer and the analyzing technique should be checked by sampling and analyzing a known concentration, such as air; the fuel factor should be reviewed and verified. An acceptability range of ±12 percent is appropriate for the F₁ factor of mixed fuels with variable fuel ratios. The level of the emission rate relative to the compliance level should be considered in determining if a retest is appropriate, i.e., if the measured emissions are much lower or much greater than the compliance limit, repetition of the test would not significantly change the compliance status of the source and would be unnecessarily time-consuming and costly.

5. Leak-Check Procedure for Orsat Analyzers

Moving an Orsat analyzer frequently causes it to leak. Therefore, an Orsat analyzer should be thoroughly leak-checked on site before the flue gas sample is introduced into it. The procedure for leak-checking an Orsat analyzer is:

5.1.1 Bring the liquid level in each pipette up to the reference mark on the capillary tubing and then close the pipette stopcock.

5.1.2 Raise the leveling bulb sufficiently to bring the confining liquid meniscus onto the graduated portion of the burette and then close the manifold stopcock.

5.1.3 Record the meniscus position.

5.1.4 Observe the meniscus in the burette and the liquid level in the pipette for movement over the next 4 minutes.

5.1.5 For the Orsat analyzer to pass the leak-check, two conditions must be met.

5.1.5.1 The liquid level in each pipette must not fall below the bottom of the capillary tubing during this 4-minute interval.

5.1.5.2 The meniscus in the burette must not change by more than 0.2 ml during this 4-minute interval.

5.1.6 If the analyzer fails the leak-check procedure, all rubber connections and stopcocks should be checked until the cause of the leak is identified. Leaking stopcocks must be disassembled, cleaned, and re-greased. Leaking rubber connections must be replaced. After the analyzer is reassembled, the leak-check procedure must be repeated.

6. Calculations

6.1 Nomenclature.

M_d = Dry molecular weight, g/g-mole (lb/lb-mole).

%EA = Percent excess air.

%CO₂ = Percent CO₂ by volume (dry basis).

%O₂ = Percent O₂ by volume (dry basis).

%CO = Percent CO by volume (dry basis).

%N₂ = Percent N₂ by volume (dry basis).

0.264 = Ratio of O₂ to N₂ in air, v/v.

0.280 = Molecular weight of N₂ or CO, divided by 100.

0.320 = Molecular weight of O₂ divided by 100.

0.440 = Molecular weight of CO, divided by 100.

6.2 Percent Excess Air. Calculate the percent excess air (if applicable), by substituting the appropriate values of percent O₂, CO₂, and N₂ (obtained from Section 4.1.3 or 4.2.4) into Equation 3-1.

% EA =

$$\frac{\%O_2 - 0.5\%CO}{0.264\%N_2 - (\%O_2 - 0.5\%CO)} \times 100$$

Equation 3-1

NOTE: The equation above assumes that ambient air is used as the source of O₂ and that the fuel does not contain appreciable amounts of N₂ (as do coke oven or blast furnace gases). For those cases when appreciable amounts of N₂ are present (coal, oil, and natural gas do not contain appreciable amounts of N₂) or when oxygen enrichment is used, alternate methods, subject to approval of the Administrator, are required.

6.3 Dry Molecular Weight. Use Equation 3-2 to calculate the dry molecular weight of the stack gas

$$M_d = 0.440(\%CO_2) + 0.320(\%O_2) + 0.280(\%N_2 + \%CO)$$

Equation 3-2

NOTE: The above equation does not consider argon in air (about 0.9 percent, molecular weight of 39.9). A negative error of about 0.4 percent is introduced. The tester may opt to include argon in the analysis using procedures subject to approval of the Administrator.

7. Bibliography

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METHOD 5

Determination of Particulate
Emissions from Stationary Sources

METHOD 5—DETERMINATION OF PARTICULATE EMISSIONS FROM STATIONARY SOURCES

1. Principle and Applicability

1.1 Principle. Particulate matter is withdrawn isokinetically from the source and collected on a glass fiber filter maintained at a temperature in the range of $120 \pm 14^\circ \text{C}$ ($248 \pm 25^\circ \text{F}$) or such other temperature as specified by an applicable subpart of the standards or approved by Administrator. U.S. Environmental Protection Agency, for a particular application. The particulate mass, which includes any material that condenses at or above the filtration temperature, is determined gravimetrically after removal of uncombined water.

1.2 Applicability. This method is applicable for the determination of particulate emissions from stationary sources.

2. Apparatus

2.1 Sampling Train. A schematic of the sampling train used in this method is shown in Figure 5-1. Complete construction details are given in APTD-0581 (Citation 2 in Bibliography); commercial models of this train are also available. For changes from APTD-0581 and for allowable modifications of the train shown in Figure 5-1, see the following subsections.

The operating and maintenance procedures for the sampling train are described in APTD-0576 (Citation 3 in Bibliography). Since correct usage is important in obtaining valid results, all users should read APTD-0576 and adopt the operating and maintenance procedures outlined in it, unless otherwise specified herein. The sampling train consists of the following components:

2.1.1 Probe Nozzle. Stainless steel (316) or glass with sharp, tapered leading edge. The angle of taper shall be $<30^\circ$ and the taper shall be on the outside to preserve a constant internal diameter. The probe nozzle shall be of the button-hook or elbow design, unless otherwise specified by the Administrator. If made of stainless steel, the nozzle shall be constructed from seamless tubing; other materials of construction may be used, subject to the approval of the Administrator.

A range of nozzle sizes suitable for isokinetic sampling should be available, e.g., 0.32 to 1.27 cm ($\frac{1}{8}$ to $\frac{1}{2}$ in.)—or larger if higher volume sampling trains are used—inside diameter (ID) nozzles in increments of 0.16 cm ($\frac{1}{16}$ in.). Each nozzle shall be calibrated according to the procedures outlined in Section 5.

2.1.2 Probe Liner. Borosilicate or quartz glass tubing with a heating system capable of maintaining a gas temperature at the exit end during sampling of $120 \pm 14^\circ \text{C}$ ($248 \pm 25^\circ \text{F}$), or such other temperature as specified by an applicable subpart of the standards or approved by the Administrator for a particular application. (The tester may opt to operate the equipment at a temperature lower than that specified.) Since the actual temperature at the outlet of the probe is not usually monitored during sampling, probes constructed according to APTD-0581 and utilizing the calibration curves of APTD-0576 (or calibrated according to the procedure outlined in APTD-0576) will be considered acceptable.

Either borosilicate or quartz glass probe liners may be used for stack temperatures up to about 480°C (900°F) quartz liners shall be used for temperatures between 48° and 900°C (900 and $1,650^\circ \text{F}$). Both types of liners may be used at higher temperature than specified for short periods of time, subject to the approval of the Administrator. The softening temperature for borosilicate is 820°C ($1,508^\circ \text{F}$), and for quartz it is $1,500^\circ \text{C}$ ($2,732^\circ \text{F}$).

Whenever practical, every effort should be made to use borosilicate or quartz glass probe liners. Alternatively, metal liners (e.g., 316 stainless steel, Incoloy 825,¹ or other corrosion resistant metals) made of seamless tubing may be used, subject to the approval of the Administrator.

2.1.3 Pitot Tube. Type S, as described in Section 2.1 of Method 2, or other device approved by the Administrator. The pitot tube shall be attached to the probe (as shown in Figure 5-1) to allow constant monitoring of the stack gas velocity. The impact (high pressure) opening plane of the pitot tube shall be even with or above the nozzle entrance plane (see Method 2, Figure 2-6b) during sampling. The Type S pitot tube assembly shall have a known coefficient, determined as outlined in Section 4 of Method 2.

¹Mention of trade names or specific product does not constitute endorsement by the Environmental Protection Agency.

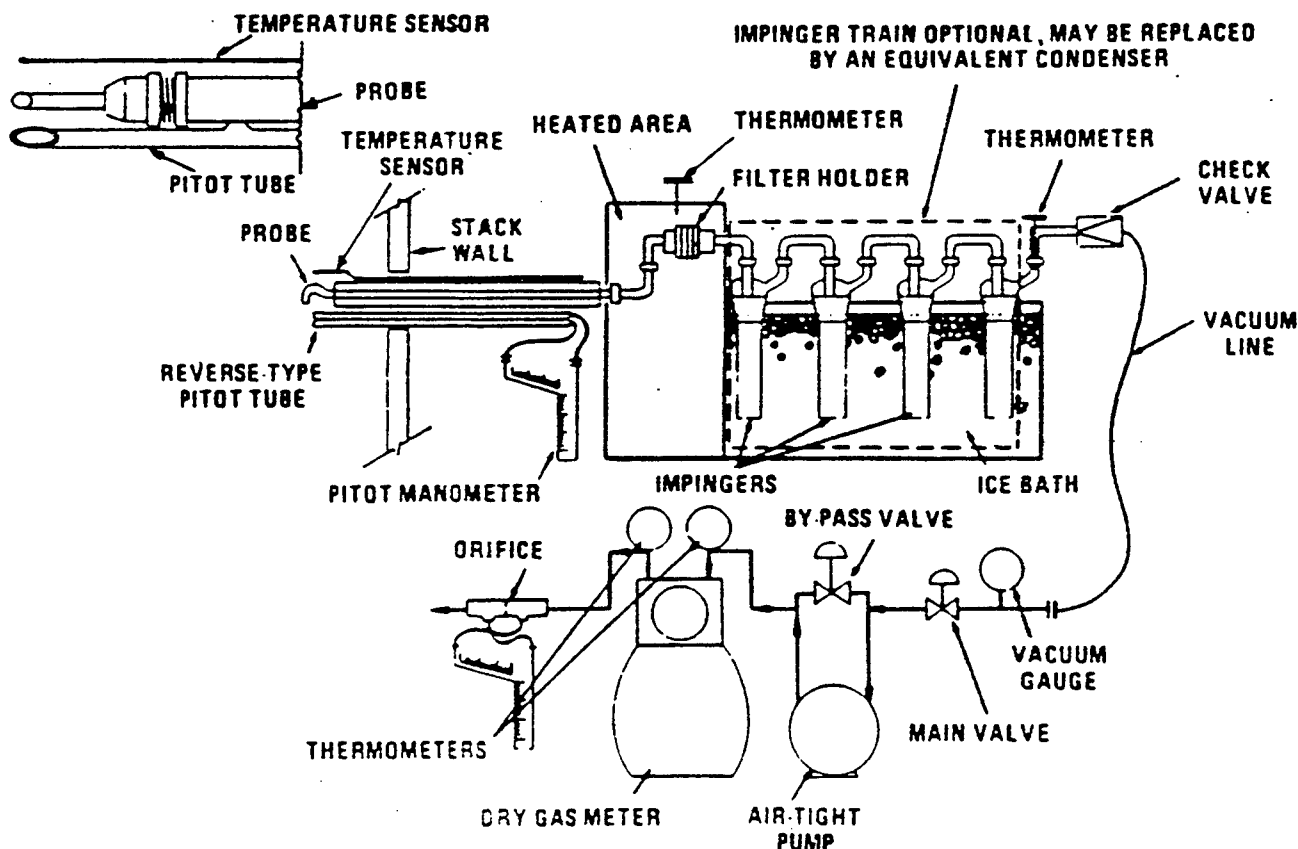


Figure 5-1. Particulate-sampling train.

2.1.4 **Differential Pressure Gauge.** Inclined manometer or equivalent device (two), as described in Section 2.2 of Method 2. One manometer shall be used for velocity head (Δp) readings, and the other, for orifice differential pressure readings.

2.1.5 **Filter Holder.** Borosilicate glass, with a glass frit filter support and a silicone rubber gasket. Other materials of construction (e.g., stainless steel, Teflon, Viton) may be used, subject to approval of the Administrator. The holder design shall provide a positive seal against leakage from the outside or around the filter. The holder shall be attached immediately at the outlet of the probe (or cyclone, if used).

2.1.6 **Filter Heating System.** Any heating system capable of maintaining a temperature around the filter holder during sampling of $120 \pm 14^\circ \text{C}$ ($248 \pm 25^\circ \text{F}$), or such other temperature as specified by an applicable subpart of the standards or approved by the Administrator for a particular application. Alternatively, the tester may opt to operate the equipment at a temperature lower than that specified. A temperature gauge capable of measuring temperature to within 3°C (5.4°F) shall be installed so that the temperature around the filter holder can be regulated and monitored during sampling. Heating systems other than the one shown in APTD-0581 may be used.

2.1.7 **Condenser.** The following system shall be used to determine the stack gas moisture content: Four impingers connected in series with leak-free ground glass fittings or any similar leak-free non-contaminating fittings. The first, third, and fourth impingers shall be of the Greenburg-Smith design, modified by replacing the tip with 1.3 cm ($\frac{1}{2}$ in.) ID glass tube extending to about 1.3 cm ($\frac{1}{2}$ in.) from the bottom of the flask. The second impinger shall be of the Greenburg-Smith design with the standard tip. Modifications (e.g., using flexible connections between the impingers, using materials other than glass, or using flexible vacuum lines to connect the filter holder to the condenser) may be used, subject to the approval of the Administrator. The first and second impingers shall contain known quantities of water (Section 4.1.3), the third shall be empty, and the fourth shall contain a known weight of silica gel, or equivalent desiccant. A thermometer, capable of measuring temperature to within 1°C (2°F) shall be placed at the outlet of the fourth impinger for monitoring purposes.

Alternatively, any system that cools the sample gas stream and allows measurement of the water condensed and moisture leaving the condenser, each to within 1 ml or 1 g may be used, subject to the approval of the Administrator. Acceptable means are to measure the condensed water either gravimetrically or volumetrically and to measure the moisture leaving the condenser by: (1) monitoring the temperature and pressure at the exit of the condenser and using Dalton's law of partial pressures; or (2) passing the sample gas stream through a tared silica gel or equivalent desiccant trap with exit lines kept below 20°C (68°F) and determining the weight gain.

If means other than silica gel are used to determine the amount of moisture leaving the condenser, it is recommended that silica gel (or equivalent) still be used between the condenser system and pump to prevent moisture condensation in the pump and metering devices and to avoid the need to make corrections for moisture in the metered volume.

NOTE: If a determination of the particulate matter collected in the impingers is desired in addition to moisture content, the impinger system described above shall be used, without modification. Individual States or control agencies requiring this information shall be contacted as to the sample recovery and analysis of the impinger contents.

2.1.8 **Metering System.** Vacuum gauge, leak-free pump, thermometers capable of measuring temperature to within 3°C (5.4°F), dry gas meter capable of measuring volume to within 2 percent, and related equipment, as shown in Figure 5-1. Other metering systems capable of maintaining sampling rates within 10 percent of isokinetic and of determining sample volumes to within 2 percent may be used, subject to the approval of the Administrator. When the metering system is used in conjunction with a pitot tube, the system shall enable checks of isokinetic rates.

Sampling trains utilizing metering systems designed for higher flow rates than that described in APTD-0581 or APDT-0576 may be used provided that the specifications of this method are met.

2.1.9 **Barometer.** Mercury aneroid, or other barometer capable of measuring atmospheric pressure to within 2.5 mm Hg (0.1 in. Hg). In many cases the barometric reading may be obtained from a nearby national weather service station, in which case the station value (which is the absolute barometric pressure) shall be requested and an adjustment for elevation differences between the weather station and sampling point shall be applied at a rate of minus 2.5 mm Hg (0.1 in. Hg) per 30 m (100 ft) elevation increase or vice versa for elevation decrease.

2.1.10 **Gas Density Determination Equipment.** Temperature sensor and pressure gauge, as described in Sections 2.3 and 2.4 of Method 2, and gas analyzer, if necessary, as described in Method 3. The temperature sensor shall, preferably, be permanently attached to the pitot tube or sampling probe in a fixed configuration, such that the tip of the sensor extends beyond the leading edge of the probe sheath and does not touch any metal. Alternatively, the sensor may be attached just prior to use in the field. Note, however, that if the temperature sensor is attached in the field, the sensor must be placed in an interference-free arrangement with respect to the Type S pitot tube openings (see Method 2, Figure 2-7). As a second alternative, if a difference of not more than 1 percent in the average velocity measurement is to be introduced, the temperature gauge need not be attached to the probe or pitot tube. (This alternative is subject to the approval of the Administrator.)

2.2 **Sample Recovery.** The following items are needed.

2.2.1 **Probe-Liner and Probe-Nozzle Brushes.** Nylon bristle brushes with stainless steel wire handles. The probe brush shall have extensions (at least as long as the probe) of stainless steel, Nylon, Teflon, or similarly inert material. The brushes shall be properly sized and shaped to brush out the probe liner and nozzle.

2.2.2 **Wash Bottles—Two.** Glass wash bottles are recommended; polyethylene wash bottles may be used at the option of the tester. It is recommended that acetone not be stored in polyethylene bottles for longer than a month.

2.2.3 **Glass Sample Storage Containers.** Chemically resistant, borosilicate glass bottles, for acetone washes, 500 ml or 1000 ml. Screw cap liners shall either be rubber-backed Teflon or shall be constructed so as to be leak-free and resistant to chemical attack by acetone. (Narrow mouth glass bottles have been found to be less prone to leakage.) Alternatively, polyethylene bottles may be used.

2.2.4 **Petri Dishes.** For filter samples, glass or polyethylene, unless otherwise specified by the Administrator.

2.2.5 **Graduated Cylinder and/or Balance.** To measure condensed water to within 1 ml or 1 g. Graduated cylinders shall have subdivisions no greater than 2 ml. Most laboratory balances are capable of weighing to the nearest 0.5 g or less. Any of these balances is suitable for use here and in Section 2.3.4.

2.2.6 **Plastic Storage Containers.** Airtight containers to store silica gel.

2.2.7 **Funnel and Rubber Policeman.** To aid in transfer of silica gel to container; not

2.2.8 **Funnel.** Glass or polyethylene, to aid in sample recovery.

2.2 **Analysis.** For analysis, the following equipment is needed.

2.3.1 **Glass Weighing Dishes.**

2.3.2 **Desiccator.**

2.3.3 **Analytical Balance.** To measure to within 0.1 mg.

2.3.4 **Balance.** To measure to within 0.5 g.

2.3.5 **Beakers.** 250 ml.

2.3.6 **Hygrometer.** To measure the relative humidity of the laboratory environment.

2.3.7 **Temperature Gauge.** To measure the temperature of the laboratory environment.

3. Reagents

3.1 **Sampling.** The reagents used in sampling are as follows:

3.1.1 **Filters.** Glass fiber filters, without organic binder, exhibiting at least 99.95 percent efficiency (<0.05 percent penetration) on 0.3-micron dioctyl phthalate smoke particles. The filter efficiency test shall be conducted in accordance with ASTM standard method D2986-71 (Reapproved 1978) (incorporated by reference—see § 60.17). Test data from the supplier's quality control program are sufficient for this purpose. In sources containing SO_2 or SO_3 , the filter material must be of a type that is unreactive to SO_2 or SO_3 . Citation 10 in Section 7 Bibliography, may be used to select the appropriate filter.

3.1.2 **Silica Gel.** Indicating type, 6 to 16 mesh. If previously used, dry at 175°C (350°F) for 2 hours. New silica gel may be used as received. Alternatively, other types of desiccants (equivalent or better) may be used, subject to the approval of the Administrator.

3.1.3 **Water.** When analysis of the material caught in the impingers is required, distilled water shall be used. Run blanks prior to field use to eliminate a high blank on test samples.

3.1.4 **Crushed Ice.**

3.1.5 **Stopcock Grease.** Acetone-insoluble, heat-stable silicone grease. This is not necessary if screw-on connectors with Teflon sleeves or similar, are used. Alternatively, other types of stopcock grease may be used, subject to the approval of the Administrator.

3.2 Sample Recovery. Acetone-reagent grade, <0.001 percent residue, in glass bottles is required. Acetone from metal containers generally has a high residue blank and should not be used. Sometimes, suppliers transfer acetone to glass bottles from metal containers; thus, acetone blanks shall be run prior to field use and only acetone with low blank values (<0.001 percent) shall be used. In no case shall a blank value of greater than 0.001 percent of the weight of acetone used be subtracted from the sample weight.

3.3 Analysis. Two reagents are required for the analysis:

3.3.1 Acetone. Same as 3.2.

3.3.2 Desiccant. Anhydrous calcium sulfate, indicating type. Alternatively, other types of desiccants may be used, subject to the approval of the Administrator.

4. Procedure

4.1 Sampling. The complexity of this method is such that, in order to obtain reliable results, testers should be trained and experienced with the test procedures.

4.1.1 Pretest Preparation. It is suggested that sampling equipment be maintained according to the procedures described in APTD-0578.

Weigh several 200 to 300 g portions of silica gel in air-tight containers to the nearest 0.5 g. Record the total weight of the silica gel plus container, on each container. As an alternative, the silica gel need not be preweighed, but may be weighed directly in the impinger or sampling holder just prior to train assembly.

Check filters visually against light for irregularities and flaws or pinhole leaks. Label filters of the proper diameter on the back side near the edge using numbering machine ink. As an alternative, label the shipping containers (glass or plastic petri dishes) and keep the filters in these containers at all times except during sampling and weighing.

Desiccate the filters at $20 \pm 5.6^\circ \text{C}$ ($68 \pm 10^\circ \text{F}$) and ambient pressure for at least 24 hours and weigh at intervals of at least 6 hours to a constant weight, i.e., 0.5 mg change from previous weighing; record results to the nearest 0.1 mg. During each weighing the filter must not be exposed to the laboratory atmosphere for a period greater than 2 minutes and a relative humidity above 50 percent. Alternatively (unless otherwise specified by the Administrator), the filters may be oven dried at 105°C (220°F) for 2 to 3 hours, desiccated for 2 hours, and weighed. Procedures other than those described, which account for relative humidity effects, may be used, subject to the approval of the Administrator.

4.1.2 Preliminary Determinations. Select the sampling site and the minimum number of sampling points according to Method 1 or as specified by the Administrator. Determine the stack pressure, temperature, and the range of velocity heads using Method 2; it is recommended that a leak-check of the pitot lines (see Method 2, Section 3.1) be performed. Determine the moisture content using Approximation Method 4 or its alternatives for the purpose of making isokinetic sampling rate settings. Determine the stack

gas dry molecular weight, as described in Method 2, Section 3.6; if integrated Method 3 sampling is used for molecular weight determination, the integrated bag sample shall be taken simultaneously with, and for the same total length of time as, the particulate sample run.

Select a nozzle size based on the range of velocity heads, such that it is not necessary to change the nozzle size in order to maintain isokinetic sampling rates. During the run, do not change the nozzle size. Ensure that the proper differential pressure gauge is chosen for the range of velocity heads encountered (see Section 2.2 of Method 2).

Select a suitable probe liner and probe length such that all traverse points can be sampled. For large stacks, consider sampling from opposite sides of the stack to reduce the length of probes.

Select a total sampling time greater than or equal to the minimum total sampling time specified in the test procedures for the specific industry such that (1) the sampling time per point is not less than 2 min (or some greater time interval as specified by the Administrator), and (2) the sample volume taken (corrected to standard conditions) will exceed the required minimum total gas sample volume. The latter is based on an approximate average sampling rate.

It is recommended that the number of minutes sampled at each point be an integer or an integer plus one-half minute, in order to avoid timekeeping errors. The sampling time at each point shall be the same.

In some circumstances, e.g., batch cycles, it may be necessary to sample for shorter times at the traverse points and to obtain smaller gas sample volumes. In these cases, the Administrator's approval must first be obtained.

4.1.3 Preparation of Collection Train. During preparation and assembly of the sampling train, keep all openings where contamination can occur covered until just prior to assembly or until sampling is about to begin.

Place 100 ml of water in each of the first two impingers, leave the third impinger empty, and transfer approximately 200 to 300 g of preweighed silica gel from its container to the fourth impinger. More silica gel may be used, but care should be taken to ensure that it is not entrained and carried out from the impinger during sampling. Place the container in a clean place for later use in the sample recovery. Alternatively, the weight of the silica gel plus impinger may be determined to the nearest 0.5 g and recorded.

Using a tweezer or clean disposable surgical gloves, place a labeled (identified) and weighed filter in the filter holder. Be sure that the filter is properly centered and the gasket properly placed so as to prevent the sample gas stream from circumventing the filter. Check the filter for tears after assembly is completed.

When glass liners are used, install the selected nozzle using a Viton A O-ring when stack temperatures are less than 260°C (500°F) and an asbestos string gasket when temperatures are higher. See APTD-0578 for details. Other connecting systems using either 316 stainless steel or Teflon ferrules may be used. When metal liners are used, install the nozzle as above or by a leak-free direct mechanical connection. Mark the probe with heat resistant tape or by some other method to denote the proper distance into the stack or duct for each sampling point.

Set up the train as in Figure 5-1, using (if necessary) a very light coat of silicone grease on all ground glass joints, greasing only the outer portion (see APTD-0578) to avoid possibility of contamination by the silicone grease. Subject to the approval of the Administrator, a glass cyclone may be used between the probe and filter holder when the total particulate catch is expected to exceed 100 mg or when water droplets are present in the stack gas.

Place crushed ice around the impingers.

4.1.4 Leak-Check Procedures.

4.1.4.1 Pretest Leak-Check. A pretest leak-check is recommended, but not required. If the tester opts to conduct the pretest leak-check, the following procedure shall be used.

After the sampling train has been assembled, turn on and set the filter and probe heating systems at the desired operating temperatures. Allow time for the temperatures to stabilize. If a Viton A O-ring or other leak-free connection is used in assembling the probe nozzle to the probe liner, leak-check the train at the sampling site by plugging the nozzle and pulling a 380 mm Hg (15 in. Hg) vacuum.

NOTE: A lower vacuum may be used, provided that it is not exceeded during the test.

If an asbestos string is used, do not connect the probe to the train during the leak-check. Instead, leak-check the train by first plugging the inlet to the filter holder (cyclone, if applicable) and pulling a 380 mm Hg (15 in. Hg) vacuum (see Note immediately above). Then connect the probe to the train and leak-check at about 25 mm Hg (1 in. Hg) vacuum; alternatively, the probe may be leak-checked with the rest of the sampling train, in one step, at 380 mm Hg (15 in. Hg) vacuum. Leakage rates in excess of 4 percent of the average sampling rate or $0.00057 \text{ m}^3/\text{min}$ (0.02 cfm), whichever is less, are unacceptable.

The following leak-check instructions for the sampling train described in APTD-0576 and APTD-0581 may be helpful. Start the pump with bypass valve fully open and coarse adjust valve, completely closed. Partially open the coarse adjust valve and slowly close the bypass valve until the desired vacuum is reached. Do not reverse direction of bypass valve; this will cause water to back up into the filter holder. If the desired vacuum is exceeded, either leak-check at this higher vacuum or end the leak-check as shown below and start over.

When the leak-check is completed, first slowly remove the plug from the inlet to the probe, filter holder, or cyclone (if applicable) and immediately turn off the vacuum pump. This prevents the water in the impingers from being forced backward into the filter holder and silica gel from being entrained backward into the third impinger.

4.1.4.2 Leak-Checks During Sample Run. If, during the sampling run, a component (e.g., filter assembly or impinger) change becomes unnecessary, a leak-check shall be conducted immediately before the change is made. The leak-check shall be done according to the procedure outlined in Section 4.1.4.1 above, except that it shall be done at a vacuum equal to or greater than the maximum value recorded up to that point in the test. If the leakage rate is found to be no greater than $0.00057 \text{ m}^3/\text{min}$ (0.02 cfm) or 4 percent of the average sampling rate (whichever is less), the results are acceptable, and no correction will need to be applied to the total volume of dry gas metered.

For each run, record the data required on a data sheet such as the one shown in Figure 5-2. Be sure to record the initial dry gas meter reading. Record the dry gas meter readings at the beginning and end of each sampling time increment, when changes in flow rates are made, before and after each leak-check, and when sampling is halted.

When the stack is under significant negative pressure (height of impinger stem), take care to close the coarse adjust valve before inserting the probe into the stack to prevent water from backing into the filter holder. If necessary, the pump may be turned on with the coarse adjust valve closed.

A single train shall be used for the entire sample run, except in cases where simultaneous sampling is required in two or more separate ducts or at two or more different locations within the same duct, or, in cases where equipment failure necessitates a change of trains. In all other situations, the use of two or more trains will be subject to the approval of the Administrator.

ni	Ambient temperature
Location	Barometric pressure
Operator	Assumed moisture, %
Date	Probe length, m (ft.)
No	Nozzle identification No.
niple box No.	Average calibrated nozzle diameter, cm (in.)
ter box No.	Probe heater setting
Meter 1114	Leak rate, m ³ /min. (cm ³ /min.)
C factor	Probe liner material
Pilot tube coefficient, Co	Static pressure, mm. Hg (in. Hg)
	Filter No.

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Note that when two or more trains are used, separate analyses of the front-half and (if applicable) impinger catches from each train shall be performed, unless identical nozzle sizes were used on all trains, in which case, the front-half catches from the individual trains may be combined (as may the impinger catches) and one analysis of front-half catch and one analysis of impinger catch may be performed. Consult with the Administrator for details concerning the calculation of results when two or more trains are used.

At the end of the sample run, turn off the coarse adjust valve, remove the probe and nozzle from the stack, turn off the pump, record the final dry gas meter reading, and conduct a post-test leak-check, as outlined in Section 4.1.4.3. Also, leak-check the pitot lines as described in Method 2, Section 3.1; the lines must pass this leak-check, in order to validate the velocity head data.

4.1.6 Calculation of Percent Isokinetic. Calculate percent isokinetic (see Calculations, Section 6) to determine whether the run was valid or another test run should be made. If there was difficulty in maintaining isokinetic rates due to source conditions, consult with the Administrator for possible variance on the isokinetic rates.

4.2 Sample Recovery. Proper cleanup procedure begins as soon as the probe is removed from the stack at the end of the sampling period. Allow the probe to cool.

When the probe can be safely handled, wipe off all external particulate matter near the tip of the probe nozzle and place a cap over it to prevent losing or gaining particulate matter. Do not cap off the probe tip tightly while the sampling train is cooling down as this would create a vacuum in the filter holder, thus drawing water from the impingers into the filter holder.

Before moving the sample train to the cleanup site, remove the probe from the sample train, wipe off the silicone grease, and cap the open outlet of the probe. Be careful not to lose any condensate that might be present. Wipe off the silicone grease from the filter inlet where the probe was fastened and cap it. Remove the umbilical cord from the last impinger and cap the impinger. If a flexible line is used between the first impinger or condenser and the filter holder, disconnect the line at the filter holder and let any condensed water or liquid drain into the impingers or condenser. After wiping off the silicone grease, cap off the filter holder outlet and impinger inlet. Either ground-glass stoppers, plastic caps, or serum caps may be used to close these openings.

Transfer the probe and filter-impinger assembly to the cleanup area. This area should be clean and protected from the wind so that the chances of contaminating or losing the sample will be minimized.

Save a portion of the acetone used for cleanup as a blank. Take 200 ml of this acetone directly from the wash bottle being used and place it in a glass sample container labeled "acetone blank."

Inspect the train prior to and during disassembly and note any abnormal conditions. Treat the samples as follows:

Container No. 1. Carefully remove the filter from the filter holder and place it in its identified petri dish container. Use a pair of tweezers and/or clean disposable surgical gloves to handle the filter. If it is necessary to fold the filter, do so such that the particulate cake is inside the fold. Carefully transfer to the petri dish any particulate matter and/or filter fibers which adhere to the filter holder gasket, by using a dry Nylon

bristle brush and/or a sharp-edged blade. Seal the container.

Container No. 2. Taking care to see that dust on the outside of the probe or other exterior surfaces does not get into the sample, quantitatively recover particulate matter or any condensate from the probe nozzle, probe fitting, probe liner, and front half of the filter holder by washing these components with acetone and placing the wash in a glass container. Distilled water may be used instead of acetone when approved by the Administrator and shall be used when specified by the Administrator; in these cases, save a water blank and follow the Administrator's directions on analysis. Perform the acetone rinses as follows:

Carefully remove the probe nozzle and clean the inside surface by rinsing with acetone from a wash bottle and brushing with a Nylon bristle brush. Brush until the acetone rinse shows no visible particles, after which make a final rinse of the inside surface with acetone.

Brush and rinse the inside parts of the Swagelok fitting with acetone in a similar way until no visible particles remain.

Rinse the probe liner with acetone by tilting and rotating the probe while squirting acetone into its upper end so that all inside surfaces will be wetted with acetone. Let the acetone drain from the lower end into the sample container. A funnel (glass or polyethylene) may be used to aid on transferring liquid washes to the container. Follow the acetone rinse with a probe brush. Hold the probe in an inclined position, squirt acetone into the upper end as the probe brush is being pushed with a twisting action through the probe; hold a sample container underneath the lower end of the probe, and catch any acetone and particulate matter which is brushed from the probe. Run the brush through the probe three times or more until no visible particulate matter is carried out with the acetone or until none remains in the probe liner on visual inspection. With stainless steel or other metal probes, run the brush through in the above prescribed manner at least six times since metal probes have small crevices in which particulate matter can be entrapped. Rinse the brush with acetone, and quantitatively collect these washings in the sample container. After the brushing, make a final acetone rinse of the probe as described above.

It is recommended that two people clean the probe to minimize sample losses. Between sampling runs, keep brushes clean and protected from contaminations.

After ensuring that all joints have been wiped clean of silicone grease, clean the inside of the front half of the filter holder by rubbing the surfaces with a Nylon bristle brush and rinsing with acetone. Rinse each surface three times or more if needed to remove visible particulate. Make a final rinse of the brush and filter holder. Carefully rinse out the glass cyclone, also (if applicable). After all acetone washings and particulate matter have been collected in the sample container, tighten the lid on the sample container so that acetone will not leak out when it is shipped to the laboratory. Mark the height of the fluid level to determine whether or not leakage occurred during transport. Label the container to clearly identify its contents.

Container No. 3. Note the color of the indicating silica gel to determine if it has been completely spent and make a notation of its condition. Transfer the silica gel from the fourth impinger to its original container and seal. A funnel may make it easier to pour the silica gel without spilling. A rubber policeman may be used as an aid in removing the silica gel from the impinger. It is not necessary to remove the small amount of dust particles that may adhere to the impinger wall and are difficult to remove. Since the gain in weight is to be used for moisture calculations, do not use any water or other liquids to transfer the silica gel. If a balance is available in the field, follow the procedure for container No. 3 in Section 4.3.

Impinger Water. Treat the impingers as follows: Make a notation of any color or film in the liquid catch. Measure the liquid which is in the first three impingers to within ± 1 ml by using a graduated cylinder or by weighing it to within ± 0.5 g by using a balance (if one is available). Record the volume or weight of liquid present. This information is required to calculate the moisture content of the effluent gas.

Discard the liquid after measuring and recording the volume or weight, unless analysis of the impinger catch is required (see Note, Section 2.1.7).

If a different type of condenser is used, measure the amount of moisture condensed either volumetrically or gravimetrically.

Whenever possible, containers should be shipped in such a way that they remain upright at all times.

4.3 Analysis. Record the data required on a sheet such as the one shown in Figure 5-3. Handle each sample container as follows:

FIGURE 5-3—ANALYTICAL DATA

Plant _____
Date _____
Run No. _____
Filter No. _____
Amount liquid lost during transport _____
Acetone blank volume, ml _____
Acetone wash volume, ml _____
Acetone blank concentration, mg/mg (equation 5-4) _____
Acetone wash blank, mg (equation 5-5) _____

Container number	Weight of particulate collected, mg		
	Final weight	Tare weight	Weight gain
1			
2			

Total _____
Less acetone blank _____
Weight of particulate matter _____

	Volume of liquid water collected	
	Impinger volume, ml	Silica gel weight, g
Final		
Initial		
Liquid collected		
Total volume collected		

*Convert weight of water to volume by dividing total weight increase by density of water (1 g/ml).

Increase, g
(1 g/ml) = Volume water, ml

Container No. 1. Leave the contents in the shipping container or transfer the filter and any loose particulate from the sample container to a tared glass weighing dish. Desiccate for 24 hours in a desiccator containing anhydrous calcium sulfate. Weigh to a constant weight and report the results to the nearest 0.1 mg. For purposes of this Section 4.3, the term "constant weight" means a difference of no more than 0.5 mg or 1 percent of total weight less tare weight, whichever is greater, between two consecutive weighings, with no less than 6 hours of desiccation time between weighings.

Alternatively, the sample may be oven dried at 105° C (220° F) for 2 to 3 hours, cooled in the desiccator, and weighed to a constant weight, unless otherwise specified by the Administrator. The tester may also opt to oven dry the sample at 105° C (220° F) for 2 to 3 hours, weigh the sample, and use this weight as a final weight.

Container No. 2. Note the level of liquid in the container and confirm on the analysis sheet whether or not leakage occurred during transport. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results. Measure the liquid in this container either volumetrically to ± 1 ml or gravimetrically to ± 0.5 g. Transfer the contents to a tared 250-ml beaker and evaporate to dryness at ambient temperature and pressure. Desiccate for 24 hours and weigh to a constant weight. Report the results to the nearest 0.1 mg.

Container No. 3. Weigh the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g using a balance. This step may be conducted in the field.

"Acetone Blank" Container. Measure acetone in this container either volumetrically or gravimetrically. Transfer the acetone to a tared 250-ml beaker and evaporate to dryness at ambient temperature and pressure. Desiccate for 24 hours and weigh to a constant weight. Report the results to the nearest 0.1 mg.

NOTE: At the option of the tester, the contents of Container No. 2 as well as the acetone blank container may be evaporated at temperatures higher than ambient. If evaporation is done at an elevated temperature, the temperature must be below the boiling point of the solvent; also, to prevent "bumping," the evaporation process must be closely supervised, and the contents of the beaker must be swirled occasionally to maintain an even temperature. Use extreme care, as acetone is highly flammable and has a low flash point.

4.4 Quality Control Procedures. The following quality control procedures are suggested to check the volume metering system calibration values at the field test site prior to sample collection. These procedures are optional for the tester.

4.4.1 Meter Orifice Check. Using the calibration data obtained during the calibration procedure described in Section 5.3, determine the ΔH_0 for the metering system orifice. The ΔH_0 is the orifice pressure differential in units of in. H₂O that correlates to 0.75 cfm of air at 528°R and 29.92 in. Hg. The ΔH_0 is calculated as follows:

$$\Delta H_0 = 0.0319 \frac{T_a}{P_{atm}} \frac{\Theta}{Y \sqrt{V_0}}$$

Eq. 5-9

Where:

ΔH = Average pressure differential across the orifice meter, in. H₂O.

T_a = Absolute average dry gas meter temperature, °R.

P_{atm} = Barometric pressure, in. Hg.

Θ = Total sampling time, min.

Y = Dry gas meter calibration factor, dimensionless.

V_0 = Volume of gas sample as measured by dry gas meter, dcf.

$0.0319 = (0.0567 \text{ in. Hg}/^\circ\text{R}) \times (0.75 \text{ cfm})$

Before beginning the field test (a set of three runs usually constitutes a field test), operate the metering system (i.e., pump, volume meter, and orifice) at the ΔH_0 pressure differential for 10 minutes. Record the volume collected, the dry gas meter temperature, and the barometric pressure. Calculate a dry gas meter calibration check value, Y_c , as follows:

$$Y_c = \frac{10}{V_c} \left[\frac{0.0319 T_a}{P_{atm}} \right] \frac{1}{\Theta}$$

Eq. 5-10

Where:

Y_c = Dry gas meter calibration check value, dimensionless.

10 = 10 minutes of run time.

Compare the Y_c value with the dry gas meter calibration factor Y to determine that:

$0.97Y < Y_c < 1.03Y$

If the Y_c value is not within this range, the volume metering system should be investigated before beginning the test.

4.4.2 Calibration Critical Orifice. A calibrated critical orifice, calibrated against a wet test meter or spirometer and designed to be inserted at the inlet of the sampling meter box, may be used as a quality control check by following the procedure of Section 7.2.

5. Calibration

Maintain a laboratory log of all calibrations.

5.1 Probe Nozzle. Probe nozzles shall be calibrated before their initial use in the field. Using a micrometer, measure the inside diameter of the nozzle to the nearest 0.025 mm (0.001 in.). Make three separate measurements using different diameters each time, and obtain the average of the measurements. The difference between the high and low numbers shall not exceed 0.1 mm (0.004 in.). When nozzles become nicked, dented, or corroded, they shall be reshaped, sharpened, and recalibrated before use. Each nozzle shall be permanently and uniquely identified.

5.2 Pitot Tube. The Type S pitot tube assembly shall be calibrated according to the procedure outlined in Section 4 of Method 2.

5.3 Metering System. Before its initial use in the field, the metering system shall be calibrated according to the procedure outlined in APTD-0576. Instead of physically adjusting the dry gas meter dial readings to correspond to the wet test meter readings, calibration factors may be used to mathematically correct the gas meter dial readings to the proper values. Before calibrating the metering system, it is suggested that a leak-check be conducted. For metering systems having diaphragm pumps, the normal leak-check procedure will not detect leakages within the pump, for these cases

the following leak-check procedure is suggested: make a 10-minute calibration run at 0.0057 m³/min (0.02 cfm); at the end of the run, take the difference of the measured wet test meter and dry gas meter volumes; divide the difference by 10, to get the leak rate. The leak rate should not exceed 0.00057 m³/min (0.02 cfm).

After each field use, the calibration of the metering system shall be checked by performing three calibration runs at a single, intermediate orifice setting (based on the previous field test). With the vacuum set at the maximum value reached during the test series. To adjust the vacuum, insert a valve between the wet test meter and the inlet of the metering system. Calculate the average value of the calibration factor. If the calibration has changed by more than 5 percent, recalibrate the meter over the full range of orifice settings, as outlined in APTD-0576.

Alternative procedures, e.g., using the orifice meter coefficients, maybe used, subject to the approval of the Administrator.

NOTE: If the dry gas meter coefficient values obtained before and after a test series differ by more than 5 percent, the test series shall either be voided, or calculations for test series shall be performed using whichever meter coefficient value (i.e., before or after) gives the lower value of total sample volume.

5.3.1 Calibration Prior to Use. Before its initial use in the field, the metering system shall be calibrated as follows: Connect the metering system inlet to the outlet of a wet test meter that is accurate to within 1 percent. Refer to Figure 5.5. The wet test meter should have a capacity of 30 liters/rev (1 ft³/rev). A spirometer of 400 liters (14 ft³) or more capacity, or equivalent, may be used for this calibration, although a wet test meter is usually more practical. The wet test meter should be periodically calibrated with a spirometer or a liquid displacement meter to ensure the accuracy of the wet test meter. Spirometers or wet test meters of other sizes may be used, provided that the specified accuracies of the procedure are maintained. Run the metering system pump for about 15 minutes with the orifice manometer indicating a median reading as expected in field use to allow the pump to warm up and to permit the interior surface of the wet test meter to be thoroughly wetted. Then, at each of a minimum of three orifice manometer settings, pass an exact quantity of gas through the wet test meter and note the gas volume indicated by the dry gas meter. Also note the barometric pressure, and the temperatures of the wet test meter, the inlet of the dry gas meter, and the outlet of the dry gas meter. Select the highest and lowest orifice settings to bracket the expected field operating range of the orifice. Use a minimum volume of 0.15 m³ (5 cf) at all orifice settings. Record all the data on a form similar to Figure 5.6, and calculate Y , the dry gas meter calibration factor, and ΔH_0 , the orifice calibration factor, at each orifice setting as shown on Figure 5.6. Allowable tolerances for individual Y and ΔH_0 values are given in Figure 5.8. Use the average of the Y values in the calculations in Section 6.

5.6 Leak Check of Metering System
Shown in Figure 5-1. That portion of the sampling train from the pump to the orifice meter should be leak checked prior to initial use and after each shipment. Leakage after the pump will result in less volume being recorded than is actually sampled. The follow-



Calculations

ΔH_g = Orifice pressure differential that equates to 0.75 cfm of air @ 68°F and 29.92 inches of mercury, in. H₂O; tolerance for individual values ± 0.20 from average.

Figure 5.6. Example data sheet for calibration of metering system (English units).

ing procedure is suggested (see Figure 5-4): Close the main valve on the meter box. Insert a one-hole rubber stopper with rubber tubing attached into the orifice exhaust pipe. Disconnect and vent the low side of the orifice manometer. Close off the low side orifice tap. Pressurize the system to 13 to 18 cm (5 to 7 in.) water column by blowing into the rubber tubing. Pinch off the tubing and observe the manometer for one minute. A loss of pressure on the manometer indicates a leak in the meter box; leaks, if present, must be corrected.

5.7 Barometer. Calibrate against a mercury barometer.

6. Calculations

Carry out calculations, retaining at least one extra decimal figure beyond that of the acquired data. Round off figures after the final calculation. Other forms of the equations may be used as long as they give equivalent results.

6.1 Nomenclature

- A_n = Cross-sectional area of nozzle, m^2 (ft^2).
- B_w = Water vapor in the gas stream, proportion by volume.
- C_a = Acetone blank residue concentration, mg/mg .
- C_p = Concentration of particulate matter in stack gas, dry basis, corrected to standard conditions, $g/dscm$ ($g/dscf$).
- I = Percent of isokinetic sampling.
- L_p = Maximum acceptable leakage rate for either a pretest leak check or for a leak check following a component change; equal to $0.0057 m^3/min$ ($0.02 cfm$) or 4 percent of the average sampling rate, whichever is less.
- L_o = Individual leakage rate observed during the leak check conducted prior to the i^{th} component change ($i=1, 2, 3, \dots, n$), m^3/min (cfm).
- L_{pt} = Leakage rate observed during the post-test leak check, m^3/min (cfm).
- m_t = Total amount of particulate matter collected, mg .
- M_w = Molecular weight of water, $18.0 g/g\text{-mole}$ ($18.0 lb/lb\text{-mole}$).
- m_r = Mass of residue of acetone after evaporation, mg .
- P_{at} = Barometric pressure at the sampling site, $mm\text{ Hg}$ ($in.\text{ Hg}$).

- P_{at} = Absolute stack gas pressure, $mm\text{ Hg}$ ($in.\text{ Hg}$).
- P_{std} = Standard pressure, $760 mm\text{ Hg}$ ($29.92 in.\text{ Hg}$).
- R = Ideal gas constant, $0.06236 mm\text{ Hg}\cdot m^3/K\cdot g\text{-mole}$ ($21.85 in.\text{ Hg}\cdot ft^3/R\cdot lb\text{-mole}$).
- T_a = Absolute average dry gas meter temperature (see Figure 5-2), $^{\circ}K$ ($^{\circ}R$).
- T_s = Absolute average stack gas temperature (see Figure 5-2), $^{\circ}K$ ($^{\circ}R$).
- T_{std} = Standard absolute temperature, $293^{\circ}K$ ($528^{\circ}R$).
- V_a = Volume of acetone blank, ml .
- V_{aw} = Volume of acetone used in wash, ml .
- V_{lt} = Total volume of liquid collected in impingers and silica gel (see Figure 5-3), ml .
- V_g = Volume of gas sample as measured by dry gas meter, dcm ($dscf$).
- V_{gstd} = Volume of gas sample measured by the dry gas meter, corrected to standard conditions, $dscm$ ($dscf$).
- V_{wstd} = Volume of water vapor in the gas sample, corrected to standard conditions, scm (scf).
- v_s = Stack gas velocity, calculated by Method 2, Equation 2-9, using data obtained from Method 5, m/sec (ft/sec).
- W_r = Weight of residue in acetone wash, mg .
- Y = Dry gas meter calibration factor.
- ΔH = Average pressure differential across the orifice meter (see Figure 5-2), $mm\text{ H}_2O$ ($in.\text{ H}_2O$).
- ρ_a = Density of acetone, mg/ml (see label on bottle).

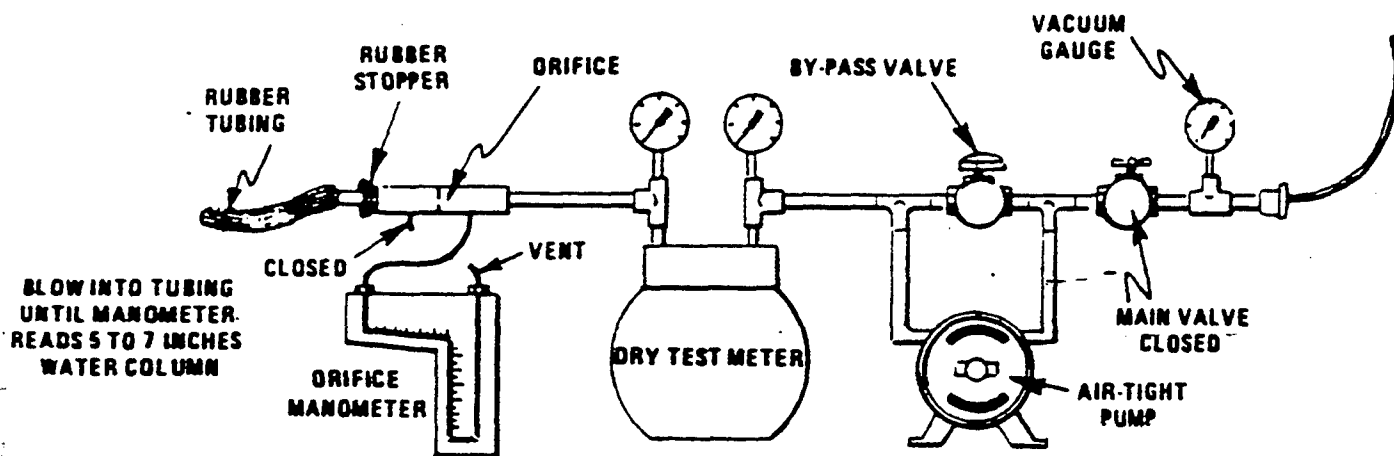


Figure 5-4. Leak check of meter box.

- ρ_w = Density of water, 0.9982 g/ml (0.002201 lb/ml).
 = Total sampling time, min.
 = Sampling time interval, from the beginning of a run until the first component change, min.
 θ_1 = Sampling time interval between two successive component changes, beginning with the interval between the first and second changes, min.
 θ_n = Sampling time interval, from the final (n^{th}) component change until the end of the sampling run, min.
 13.6 = Specific gravity of mercury.
 60 = Sec/min.
 100 = Conversion to percent.

6.2 Average dry gas meter temperature and average orifice pressure drop. See data sheet (Figure 5-2).

6.3 Dry Gas Volume. Correct the sample volume measured by the dry gas meter to standard conditions (20° C, 760 mm Hg or 68° F, 29.92 in. Hg) by using Equation 5-1.

$$V_{m(\text{std})} = V_m Y \left(\frac{T_{\text{std}}}{T_m} \right) \left[\frac{P_{\text{bar}} + \frac{\Delta H}{13.6}}{P_{\text{atm}}} \right]$$

$$= K_1 V_m Y \frac{P_{\text{bar}} + (\Delta H/13.6)}{T_m}$$

Equation 5-1

where:

- K_1 = 0.3858 °K/mm Hg for metric units
 = 17.84 °R/in. Hg for English units

Note: Equation 5-1 can be used as written unless the leakage rate observed during any of the mandatory leak checks (i.e., the post-test leak check or leak checks conducted prior to component changes) exceeds L_m . If L_m or L_n exceeds L_m , Equation 5-1 must be modified as follows:

(a) Case I. No component changes made during sampling run. In this case, replace V_m in Equation 5-1 with the expression:

$$V_m = (L_m - L_n)\theta_1$$

(b) Case II. One or more component changes made during the sampling run. In this case, replace V_m in Equation 5-1 by the expression:

$$V_m = (L_1 - L_n)\theta_1$$

$$+ \sum_{i=2}^n (L_i - L_n)\theta_i - (L_n - L_n)\theta_n$$

and substitute only for those leakage rates (L_i or L_n) which exceed L_m .

6.4 Volume of water vapor.

$$V_{w(\text{std})} = V_{w1} \left(\frac{\rho_w}{M_w} \right) \left(\frac{RT_{\text{std}}}{P_{\text{atm}}} \right) = K_2 V_{w1}$$

Equation 5-2

where:
 K_2 = 0.001333 m³/ml for metric units
 = 0.04707 ft³/ml for English units.
 6.5 Moisture Content.

$$B_m = \frac{V_{w(\text{std})}}{V_{m(\text{std})} + V_{w(\text{std})}}$$

Equation 5-3

Note: In saturated or water droplet-laden gas streams, two calculations of the moisture content of the stack gas shall be made, one from the impinger analysis (Equation 5-3), and a second from the assumption of saturated conditions. The lower of the two values of B_m shall be considered correct. The procedure for determining the moisture content based upon assumption of saturated conditions is given in the Note of Section 1.2 of Method 4. For the purposes of this method, the average stack gas temperature from Figure 5-2 may be used to make this determination, provided that the accuracy of the in-stack temperature sensor is $\pm 1^\circ$ C (2° F).

6.6 Acetone Blank Concentration.

Equation 5-4

$$C_a = \frac{m_a}{V_{a\text{std}}}$$

6.7 Acetone Wash Blank.

$$W_a = C_a V_{a\text{std}} \quad \text{Equation 5-5}$$

6.8 Total Particulate Weight. Determine the total particulate catch from the sum of the weights obtained from containers 1 and 2 less the acetone blank (see Figure 5-3).

Note: Refer to Section 4.1.3 to assist in calculation of results involving two or more filter assemblies or two or more sampling trains.

6.9 Particulate Concentration.

$$C_p = (0.001 \text{ g/mg}) (m_p / V_{m(\text{std})}) \quad \text{Equation 5-6}$$

6.10 Conversion Factors:

From	To	Multiplying by
scf	m ³	0.02832
g/N	g/N	15.43
g/N	lb/N	2.205 x 10 ⁻³
g/N	g/m ³	35.31
g	mg	1000

6.11 Isokinetic Variation.

6.11.1 Calculation From Raw Data.

$$I = \frac{V_m Y}{100 T_m [K_2 V_{w1} + (\frac{1}{T_m} (P_{\text{bar}} + \Delta H/13.6))]} \quad \text{Equation 5-7}$$

where:

- K_2 = 0.003454 mm Hg-m³/ml-°K for metric units.
 = 0.002669 in. Hg-ft³/ml-°R for English units.

6.11.2 Calculation From Intermediate Values.

$$I = \frac{T_m V_{m(\text{std})} P_{\text{atm}} 100}{T_{\text{std}} V_m \theta_1 A_s P_m (1 - B_m)}$$

$$= K_3 \frac{T_m V_{m(\text{std})}}{P_m V_m \theta_1 (1 - B_m)}$$

Equation 5-8

where:

- K_3 = 4.320 for metric units
 = 0.09450 for English units.

6.12 Acceptable Results. If 90 percent $\leq I \leq 110$ percent, the results are acceptable. If the particulate results are low in comparison to the standard, and I is over 110 percent or less than 90 percent, the Administrator may accept the results. Citation 4 in the bibliography section can be used to make acceptability judgments. If I is judged to be unacceptable, reject the particulate results and repeat the test.

6.13 Stack Gas Velocity and Volumetric Flow Rate. Calculate the average stack gas velocity and volumetric flow rate, if needed, using data obtained in this method and the equations in Sections 5.2 and 5.3 of Method 2.

7. Alternative Procedures

7.1 Dry Gas Meter as a Calibration Standard. A dry gas meter may be used as a calibration standard for volume measurements in place of the wet test meter specified in Section 5.3, provided that it is calibrated initially and recalibrated periodically as follows:

7.1.1 Standard Dry Gas Meter Calibration.

7.1.1.1 The dry gas meter to be calibrated and used as a secondary reference meter should be of high quality and have an appropriately sized capacity, e.g., 3 liters/rev (0.1 ft³/rev). A spirometer (400 liters or more capacity), or equivalent, may be used for this calibration, although a wet test meter is usually more practical. The wet test meter should have a capacity of 30 liters/rev (1 ft³/rev) and capable of measuring volume to within ± 1.0 percent. Wet test meters should be checked against a spirometer or a liquid displacement meter to ensure the accuracy of the wet test meter. Spirometers or wet test meters of other sizes may be used, provided that the specified accuracies of the procedure are maintained.

7.1.1.2 Set up the components as shown in Figure 5.7. A spirometer, or equivalent, may be used in place of the wet test meter in the system. Run the pump for at least 5 minutes at a flow rate of about 10 liters/min (0.35 cfm) to condition the interior surface of the wet test meter. The pressure drop indicated by the manometer at the inlet side of the dry gas meter should be minimized (no greater than 100 mm H₂O (4 in. H₂O) at a flow rate of 30 liters/min (1 cfm)). This can be accomplished by using large diameter tubing connections and straight pipe fittings.

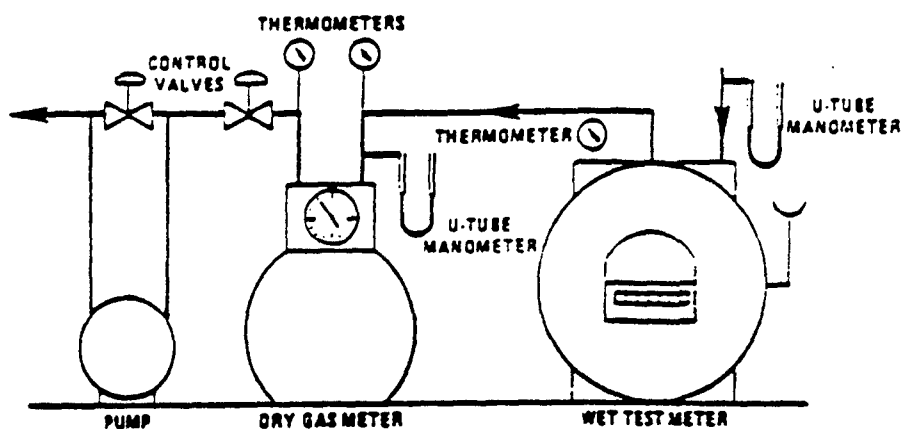


Figure 5.7 . Equipment arrangement for dry-gas meter calibration.

7.1.1.3 Collect the data as shown in the example data sheet (see Figure 5-8). Make triplicate runs at each of the flow rates and at no less than five different flow rates. The

range of flow rates should be between 10 and 34 liters/min (0.35 and 1.2 cfm) or over the expected operating range.

DATE: _____

DRY GAS METER IDENTIFICATION: _____

BAROMETRIC PRESSURE (P_b): _____ in. Hg

APPROXIMATE FLOW RATE (\bar{Q}) cfm	SPIROMETER (WET METER) GAS VOLUME (V_s) ft ³	DRY GAS METER VOLUME (V_{dg}) ft ³	TEMPERATURES				DRY GAS METER PRESSURE (Δp) in. H ₂ O	TIME (Θ) min.	FLOW RATE (Q) cfm	METER METER COEFFICIENT (Y_{dt})	AVERAGE METER COEFFICIENT (\bar{Y}_{dt})
			SPIROMETER (WET METER) (t_s) °F	DRY GAS METER							
				INLET (t_i) °F	OUTLET (t_o) °F	AVERAGE (\bar{t}_d) °F					
0.40											
0.50											
0.80											
1.00											
1.20											

$$Q = 17.85 \cdot \frac{V_s}{\Theta} \cdot \frac{P_b}{(t_s + 460)}$$

$$Y_{ds} = \frac{V_s}{V_{dg}} \cdot \frac{(t_d + 460)}{(t_s + 460)} \cdot \frac{P_b}{(P_b + \frac{\Delta p}{13.6})}$$

Figure 5-8 Example data sheet for calibration of a standard dry gas meter for method 5 sampling equipment (English units).

7.1.1.4 Calculate flow rate, Q , for each run using the wet test meter gas volume, V_w , and the run time, θ . Calculate the dry gas meter coefficient, Y_m , for each run. These calculations are as follows:

$$Q = K_1 \frac{P_w}{t_w + t_m} \frac{V_w}{\theta}$$

$$Y_m = \frac{V_w}{V_m} \frac{(t_w + t_m)}{(t_w + t_m)} \frac{P_w}{\left(P_w + \frac{\Delta P}{13.6} \right)}$$

Where:

K_1 = 0.3858 for international system of units (SI); 17.64 for English units.

V_w = Wet test meter volume, liters (ft³).

V_m = Dry gas meter volume, liters (ft³).

t_w = Average dry gas meter temperature, °C (°F).

t_m = 273° C for SI units; 460° F for English units.

t_w = Average wet test meter temperature, °C (°F).

P_w = Barometric pressure, mm Hg (in. Hg).

ΔP = Dry gas meter inlet differential pressure, mm H₂O (in. H₂O).

θ = Run time, min.

7.1.1.5 Compare the three Y_m values at each of the flow rates and determine the maximum and minimum values. The difference between the maximum and minimum values at each flow rate should be no greater than 0.030. Extra sets of triplicate runs may be made in order to complete this requirement. In addition, the meter coefficients should be between 0.95 and 1.05. If these specifications cannot be met in three sets of successive triplicate runs, the meter is not suitable as a calibration standard and should not be used as such. If these specifications are met, average the three Y_m values at each flow rate resulting in five average meter coefficients, \bar{Y}_m .

7.1.1.6 Prepare a curve of meter coefficient, \bar{Y}_m , versus flow rate, Q , for the dry gas meter. This curve shall be used as a reference when the meter is used to calibrate other dry gas meters and to determine whether recalibration is required.

7.1.2 Standard Dry Gas Meter Recalibration.

7.1.2.1 Recalibrate the standard dry gas meter against a wet test meter or spirometer annually or after every 200 hours of operation, whichever comes first. This require-

ment is valid provided the standard dry gas meter is kept in a laboratory and, if transported, cared for as any other laboratory instrument. Abuse to the standard meter may cause a change in the calibration and will require more frequent recalibrations.

7.1.2.2 As an alternative to full recalibration, a two-point calibration check may be made. Follow the same procedure and equipment arrangement as for a full recalibration, but run the meter at only two flow rates (suggested rates are 14 and 28 liters/min (0.5 and 1.0 cfm)). Calculate the meter coefficients for these two points, and compare the values with the meter calibration curve. If the two coefficients are within ± 1.5 percent of the calibration curve values at the same flow rates, the meter need not be recalibrated until the next date for a recalibration check.

7.2 Critical Orifices As Calibration

Standards. Critical orifices may be used as calibration standards in place of the wet test meter specified in Section 5.3, provided that they are selected, calibrated, and used as follows:

7.2.1 Section of Critical Orifices.

7.2.1.1 The procedure that follows describes the use of hypodermic needles or stainless steel needle tubings which have been found suitable for use as critical orifices. Other materials and critical orifice designs may be used provided the orifices act as true critical orifices; i.e., a critical vacuum can be obtained, as described in Section 7.2.2.3. Select five critical orifices that are appropriately sized to cover the range of flow rates between 10 and 34 liters/min or the expected operating range. Two of the critical orifices should bracket the expected operating range.

A minimum of three critical orifices will be needed to calibrate a Method 5 dry gas meter (DCM); the other two critical orifices can serve as spares and provide better selection for bracketing the range of operating flow rates. The needle sizes and tubing lengths shown below give the following approximate flow rates:

Gauge/cm	Flow rate (liters/min)	Gauge/cm	Flow rate (liters/min)
12/7.6	32.56	14/2.5	18.54
12/10.2	30.02	14/5.1	17.27
13/2.5	25.77	14/7.6	16.14
13/5.1	23.50	15/3.2	14.16
13/7.6	22.37	15/7.6	11.61
13/10.2	20.67	15/10.2	10.48

7.2.1.2 These needles can be adapted to a Method 5 type sampling train as follows: Insert a serum bottle stopper, 13- by 20-mm sleeve type, into a 1/4-inch Swagelok quick connect. Insert the needle into the stopper as shown in Figure 5-9.

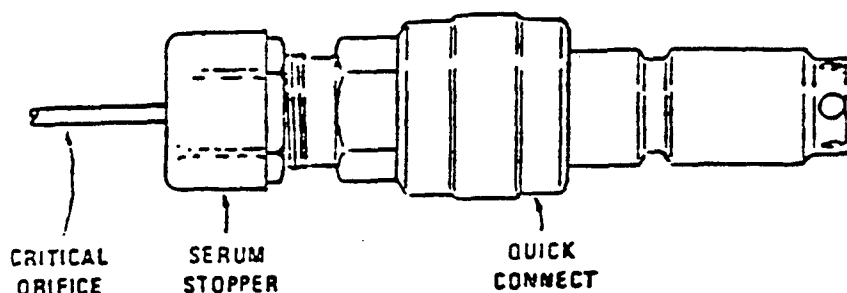


Figure 5-9. Critical orifice adaptation to Method 5 metering system.

7.2.2 Critical Orifice Calibration. The procedure described in this section uses the Method 5 meter box configuration with a DGM as described in Section 2.1.8 to calibrate the critical orifices. Other schemes may be used, subject to the approval of the Administrator.

7.2.2.1 Calibration of Meter Box. The critical orifices must be calibrated in the same configuration as they will be used; i.e., there should be no connections to the inlet of the orifice.

7.2.2.1.1 Before calibrating the meter box, leak check the system as follows: Fully open the coarse adjust valve, and completely close the by-pass valve. Plug the inlet. Then turn on the pump, and determine whether there is any leakage. The leakage rate shall be zero; i.e., no detectable movement of the DGM dial shall be seen for 1 minute.

7.2.2.1.2 Check also for leakages in that portion of the sampling train between the pump and the orifice meter. See Section 5.6 for the procedure; make any corrections, if necessary. If leakage is detected, check for

cracked gaskets, loose fittings, worn O-rings, etc., and make the necessary repairs.

7.2.2.1.3 After determining that the meter box is leakless, calibrate the meter box according to the procedure given in Section 5.3. Make sure that the wet test meter meets the requirements stated in Section 7.1.1.1. Check the water level in the wet test meter. Record the DGM calibration factor, Y.

7.2.2.2 Calibration of Critical Orifices. Set up the apparatus as shown in Figure 5-10. BILLING CODE 6699-66-01

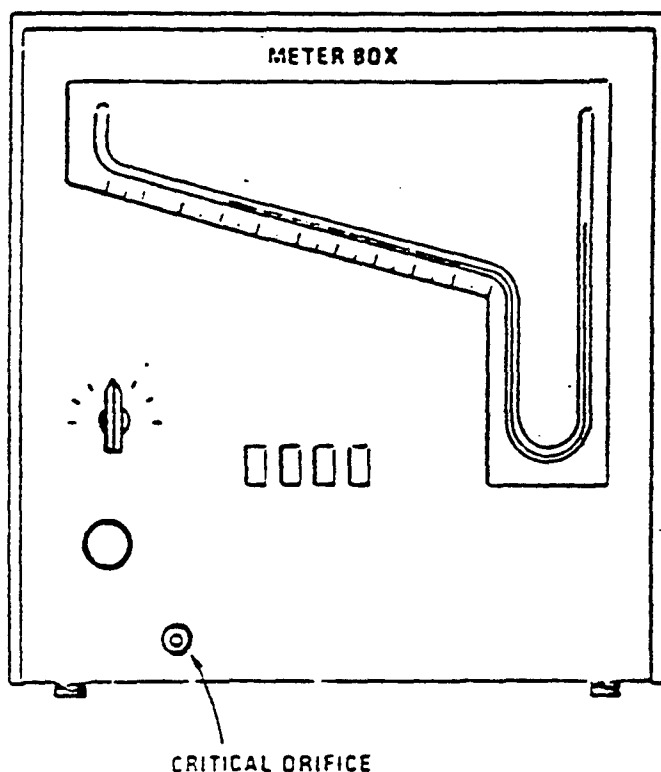


Figure 5-10. Apparatus setup.

7.2.2.2.1 Allow a warm-up time of 15 minutes. This step is important to equilibrate the temperature conditions through the DGM.

7.2.2.2.2 Leak check the system as in Section 7.2.2.1.1. The leakage rate shall be zero.

7.2.2.2.3 Before calibrating the critical orifice, determine its suitability and the appropriate operating vacuum as follows: Turn on the pump, fully open the coarse adjust valve, and adjust the by-pass valve to give a vacuum reading corresponding to about half of atmospheric pressure. Observe the meter box orifice manometer reading, H . Slowly increase the vacuum reading until a stable reading is obtained on the meter box orifice manometer. Record the critical vacuum for each orifice.

Orifices that do not reach a critical value shall not be used.

7.2.2.2.4 Obtain the barometric pressure using a barometer as described in Section 2.1.9. Record the barometric pressure, P_{bar} , in mm Hg (in. Hg).

7.2.2.2.5 Conduct duplicate runs at a vacuum of 25 to 50 mm Hg (1 to 2 in. Hg) above the critical vacuum. The runs shall be at least 5 minutes each. The DGM volume readings shall be in increments of 0.00283 m³ (0.1 ft³) or in increments of complete revolutions of the DGM. As a guideline, the times should not differ by more than 3.0 seconds (this includes allowance for changes in the DGM temperatures) to achieve ± 0.5 percent in K' . Record the information listed in Figure 5-11.

7.2.2.2.6 Calculate K' using Equation 5-9.

K' = Critical orifice coefficient.

T_{amb} = Absolute ambient temperature, °K (°R).

Average the K' values. The individual K' values should not differ by more than ± 0.5 percent from the average.

$$K' = \frac{K_1 V_m Y (P_{bar} + \Delta H/13.6) \sqrt{T_{amb}}}{P_{vac} T_{m\phi}} \quad \text{Eq. 5-9}$$

$$\frac{(\text{m}^3)(^\circ\text{K})^{1/2}}{(\text{mm. Hg})(\text{min})} \left[\frac{(\text{ft}^3)(^\circ\text{R})^{1/2}}{(\text{in. Hg})(\text{min})} \right]$$

Sections 7.2.2.2.1 to 7.2.2.2.5. Record the information listed in Figure 5.12.

7.2.3 Using the Critical Orifices as Calibration Standards.

7.2.3.1 Record the barometric pressure.

Date _____ Train ID _____ DGM cal. factor _____ Critical orifice ID _____

Dry gas meter	Run No.	
	1	2
Final reading _____ m ³ (ft ³)		
Initial reading _____ m ³ (ft ³)		
Difference, V_m _____ m ³ (ft ³)		
Inlet/Outlet temperatures:		
Initial _____ °C (°F) _____ / _____ /		
Final _____ °C (°F) _____ / _____ /		
Avg. _____ °C (°F) _____		
Temperature, T_m _____		
Time, Θ _____ min/sec _____ / _____ /		
Orifice man. rdg., ΔH , _____ mm (in.) H ₂ O		
Bar. pressure, P_{bar} _____ mm (in.) Hg		
Ambient temperature, T_{amb} _____ °C (°F) _____		
Pump vacuum _____ mm (in.) Hg		
K' factor _____		
Average _____		

Figure 5-11. Data sheet for determining K' factor.

7.2.3.2 Calibrate the metering system according to the procedure outlined in

7.2.3.3 Calculate the standard volumes of air passed through the DGM and the critical orifices, and calculate the DGM calibration factor, Y , using the equations below:

$$V_m(\text{std}) = K_1 V_m \frac{P_{bar} + (\Delta H/13.6)}{T_m} \quad \text{Eq. 5-10}$$

$$V_m(\text{std}) = K' \frac{P_{vac} \Theta}{T_{amb}} \quad \text{Eq. 5-11}$$

$$Y = \frac{V_m(\text{std})}{V_m(\text{std})} \quad \text{Eq. 5-12}$$

where:

$V_m(\text{std})$ = Volume of gas sample passed through the critical orifice, corrected to standard conditions, dsm³ (dscf).

K_1 = 0.3856 °K/mm Hg for metric units = 17.64 °R/in. Hg for English units.

7.2.3.4 Average the DGM calibration values for each of the flow rates. The calibration factor, Y , at each of the flow rates should not differ by more than ± 2 percent from the average.

7.2.3.5 To determine the need for recalibrating the critical orifices, compare the DGM Y factors obtained from two adjacent orifices each time a DGM is calibrated; for example, when checking 13/2.5, use orifices 12/10.2 and 13/5.1. If any critical orifice yields a DGM Y factor differing by more than 2 percent from the others, recalibrate the critical orifice according to Section 7.2.2.2.

Date _____ Train ID _____ Critical orifice ID _____ Critical orifice K' fac. _____

Dry gas meter	Run No.	
	1	2
Final reading _____ m ³ (ft ³)		
Initial reading _____ m ³ (ft ³)		
Difference, V_m _____ m ³ (ft ³)		
Inlet/Outlet temperatures:		
Initial _____ °C (°F) _____ / _____ /		
Final _____ °C (°F) _____ / _____ /		
Avg. _____ °C (°F) _____		
Temperature, T_m _____		
Time, Θ _____ min/sec _____ / _____ /		
Orifice man. rdg., ΔH , _____ mm (in.) H ₂ O		
Bar. pressure, P_{bar} _____ mm (in.) Hg		
Ambient temperature, T_{amb} _____ °C (°F) _____		
Pump vacuum _____ mm (in.) Hg		
$V_m(\text{std})$ _____ m ³ (ft ³)		
$V_m(\text{std})$ _____ m ³ (ft ³)		
DGM cal. factor, Y _____		

Figure 5-12. Data sheet for determining DGM Y factor.

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[FR Doc. 87-6551 Filed 3-25-87; 8:45 am]

METHOD 8

Determination of Sulfuric Acid
Mist and Sulfur Dioxide Emissions
from Stationary Sources

METHOD 8—DETERMINATION OF SULFURIC ACID MIST AND SULFUR DIOXIDE EMISSIONS FROM STATIONARY SOURCES

1. Principle and Applicability

1.1 Principle. A gas sample is extracted isokinetically from the stack. The sulfuric acid mist (including sulfur trioxide) and the sulfur dioxide are separated, and both fractions are measured separately by the barium-thorin titration method.

1.2 Applicability. This method is applicable for the determination of sulfuric acid mist (including sulfur trioxide) and in the absence of other particulate matter) and sulfur dioxide emissions from stationary sources. Collaborative tests have shown that the minimum detectable limits of the method are 0.05 milligrams/cubic meter (0.03×10^{-3} pounds/cubic foot) for sulfur trioxide and 1.2 mg/m^3 ($0.74 \times 10^{-3} \text{ lb/ft}^3$) for sulfur dioxide. No upper limits have been established. Based on theoretical calculations for 200 milliliters of 3 percent hydrogen peroxide solution, the upper concentration limit for sulfur dioxide in a 1.0 m^3 (35.3 ft^3) gas sample is about $12,500 \text{ mg/m}^3$ ($7.7 \times 10^{-3} \text{ lb/ft}^3$). The upper limit can be extended by increasing the quantity of peroxide solution in the impingers.

Possible interfering agents of this method are fluorides, free ammonia, and dimethyl aniline. If any of these interfering agents are present (this can be determined by knowledge of the process), alternative methods, subject to the approval of the Administrator, U. S. E. P. A., are required.

Filterable particulate matter may be determined along with SO_2 and SO_3 (subject to the approval of the Administrator) by inserting a heated glass fiber filter between the probe and isopronanol impinger (see Section 2.1 of method 6.) If this option is chosen, particulate analysis is gravimetric only; H_2SO_4 acid mist is not determined separately.

2. Apparatus

2.1 Sampling. A schematic of the sampling train used in this method is shown in Figure 8-1: it is similar to the Method 5 train except that the filter position is different and the filter holder does not have to be heated. Commercial models of this train are available. For those who desire to build their own, however, complete construction details are described in APTD-0581. Changes from the APTD-0581 document and allowable modifications to Figure 8-1 are discussed in the following subsections.

The operating and maintenance procedures for the sampling train are described in APTD-0576. Since correct usage is important in obtaining valid results, all users should read the APTD-0576 document and adopt the operating and maintenance procedures outlined in it, unless otherwise specified herein. Further details and guidelines on operation and maintenance are given in Method 5 and should be read and followed whenever they are applicable.

2.1.1 Probe Nozzle. Same as Method 5, Section 2.1.1.

2.1.2 Probe Liner. Borosilicate or quartz glass, with a heating system to prevent visible condensation during sampling. Do not use metal probe liners.

2.1.3 Pitot Tube. Same as Method 5, Section 2.1.3.

2.1.4 Differential Pressure Gauge. Same as Method 5, Section 2.1.4.

2.1.5 Filter Holder. Borosilicate glass, with a glass frit filter support and a silicone rubber gasket. Other gasket materials, e.g., Teflon or Viton, may be used subject to the approval of the Administrator. The holder design shall provide a positive seal against leakage from the outside or around the filter. The filter holder shall be placed between the first and second impingers. Note: Do not heat the filter holder.

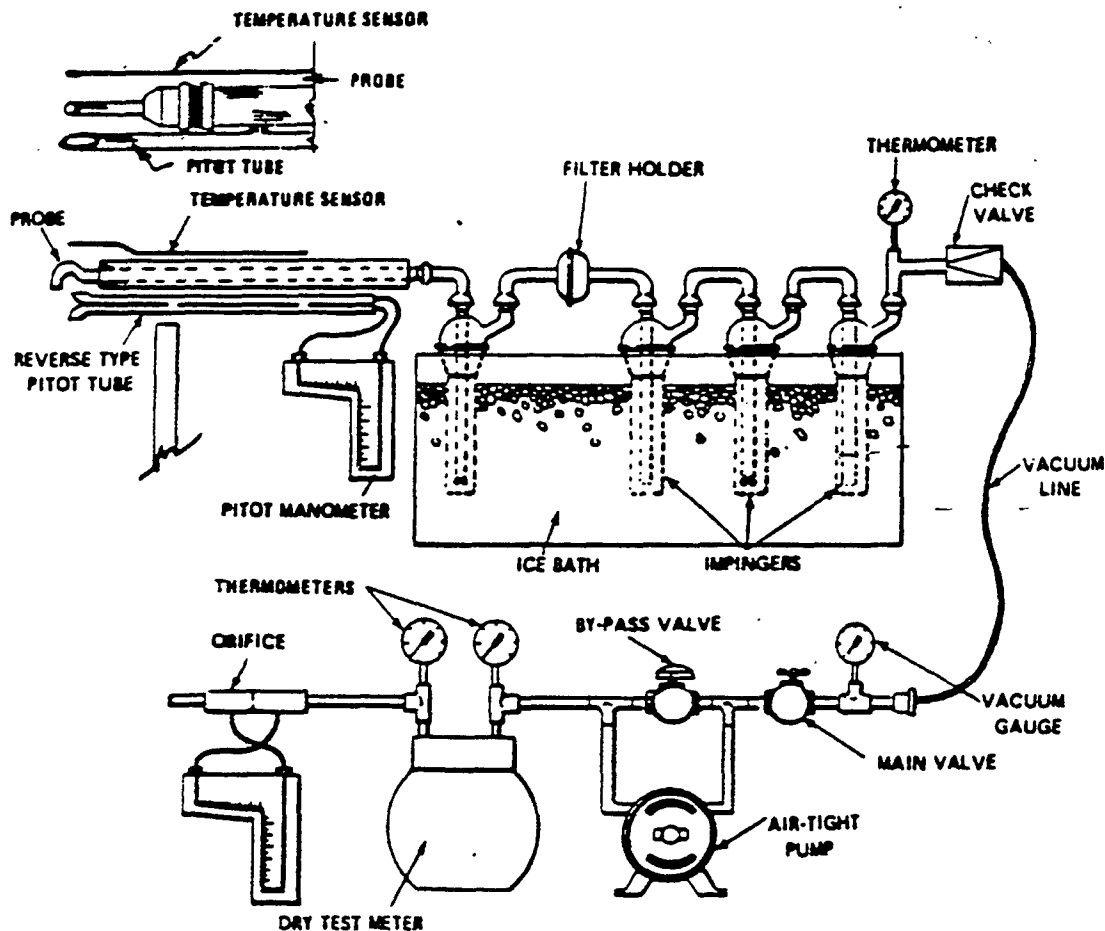


Figure 8-1. Sulfuric acid mist sampling train.

2.3.6 Dropping Bottle. To add Indicator solution, 125-ml size.

NOTE: Experience has shown that only A.C.S. grade isopropanol is satisfactory. Tests have shown that isopropanol obtained from commercial sources occasionally has peroxide impurities that will cause erroneously high sulfuric acid mist measurement. Use the following test for detecting peroxides in each lot of isopropanol: Shake 10 ml of the isopropanol with 10 ml of freshly prepared 10 percent potassium iodide solution. Prepare a blank by similarly treating 10 ml of distilled water. After 1 minute, read the absorbance on a spectrophotometer at 332 nanometers. If the absorbance exceeds 0.1, the isopropanol shall not be used. Peroxides may be removed from isopropanol by redistilling, or by passage through a column of activated alumina. However, reagent-grade

4. Procedure

SCHEMATIC OF STACK CROSS SECTION

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4.1 Sampling.

4.1.1 Pretest Preparation. Follow the procedure outlined in Method 5, Section 4.1.1. Filters should be inspected, but need not be desiccated, weighed, or identified. If the effluent gas can be considered dry, i.e., moisture free, the silica gel need not be weighed.

4.1.2 Preliminary Determinations. Follow the procedure outlined in Method 5, Section 4.1.2.

4.1.3 Preparation of Collection Train. Follow the procedure outlined in Method 5, Section 4.1.3 (except for the second paragraph and other obviously inapplicable parts) and use Figure 8-1 instead of Figure 5-1. Replace the second paragraph with: Place 100 ml of 80 percent isopropanol in the first impinger, 100 ml of 3 percent hydrogen peroxide in both the second and third impingers; retain a portion of each reagent for use as a blank solution. Place about 200g of silica gel in the fourth impinger.

NOTE: If moisture content is to be determined by impinger analysis, weigh each of the first three impingers (plus absorbing solution) to the nearest 0.5 g and record these weights. The weight of the silica gel (or silica gel plus container) must also be determined to the nearest 0.5 g and recorded.

4.1.4 Pretest Leak-Check Procedure. Follow the basic procedure outlined in Method 5, Section 4.1.4.1, noting that the probe heater shall be adjusted to the minimum temperature required to prevent condensation, and also that verbiage such as, "... plugging the inlet to the filter holder ..." shall be replaced by, "... plugging the inlet to the first impinger ..." The pretest leak-check is optional.

4.1.5 Train Operation. Follow the basic procedures outlined in Method 5, Section 4.1.5, in conjunction with the following special instructions. Data shall be recorded on a sheet similar to the one in Figure 8-2. The sampling rate shall not exceed 0.030 m³/min (1.0 cfm) during the run. Periodically during the test, observe the connecting line between the probe and first impinger for signs of condensation. If it does occur, adjust the probe heater setting upward to the minimum temperature required to prevent condensation. If component changes become necessary during a run, a leak-check shall be done immediately before each change, according to the procedure outlined in Section 4.1.4.2 of Method 5 (with appropriate modifications, as mentioned in Section 4.1.4 of this method); record all leak rates. If the leakage rate(s) exceed the specified rate, the tester shall either void the run or shall plan to correct the sample volume as outlined in section 6.3 of Method 5. Immediately after component changes, leak-checks are optional. If these leak-checks are done, the procedure outlined in Section 4.1.4.1 of Method 5 (with appropriate modifications) shall be used.

After turning off the pump and recording the final readings at the conclusion of each run, remove the probe from the stack. Conduct a post-test (mandatory) leak-check as in Section 4.1.4.3 of Method 5 (with appropriate modification) and record the leak rate. If the post-test leakage rate exceeds the specified acceptable rate, the tester shall either correct the sample volume, as outlined in Section 6.3 of Method 5, or shall void the run.

Drain the ice bath and, with the probe disconnected, purge the remaining part of the train by drawing clean ambient air through the system for 15 minutes at the average flow rate used for sampling.

NOTE: Clean ambient air can be provided by passing air through a charcoal filter. At the option of the tester, ambient air (without cleaning) may be used.

4.1.6 Calculation of Percent Isokinetic. Follow the procedure outlined in Method 5, Section 4.1.6.

4.2 Sample Recovery.

4.2.1 Container No. 1. If a moisture content analysis is to be done, weigh the first impinger plus contents to the nearest 0.5 g and record this weight.

Transfer the contents of the first impinger to a 250-ml graduated cylinder. Rinse the probe, first impinger, all connecting glassware before the filter, and the front half of the filter holder with 80 percent isopropanol. Add the rinse solution to the cylinder. Dilute to 250 ml with 80 percent isopropanol. Add the filter to the solution, mix, and transfer to the storage container. Protect the solution against evaporation. Mark the level of liquid on the container and identify the sample container.

4.2.2 Container No. 2. If a moisture content analysis is to be done, weigh the second and third impingers (plus contents) to the nearest 0.5 g and record these weights. Also, weigh the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g.

Transfer the solutions from the second and third impingers to a 1000-ml graduated cylinder. Rinse all connecting glassware (including back half of filter holder) between the filter and silica gel impinger with deionized, distilled water, and add this rinse water to the cylinder. Dilute to a volume of 1000 ml with deionized, distilled water. Transfer the solution to a storage container. Mark the level of liquid on the container. Seal and identify the sample container.

4.3 Analysis.

Note the level of liquid in containers 1 and 2, and confirm whether or not any sample was lost during shipment; note this on the analytical data sheet. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results.

4.3.1 Container No. 1. Shake the container holding the isopropanol solution and the filter. If the filter breaks up, allow the fragments to settle for a few minutes before removing a sample. Pipette a 100-ml aliquot of this solution into a 250-ml Erlenmeyer flask, add 2 to 4 drops of thion indicator, and titrate to a pink endpoint using 0.0100 N barium perchlorate. Repeat the titration with a second aliquot of sample and average the titration values. Replicate titrations must agree within 1 percent or 0.2 ml, whichever is greater.

4.3.2 Container No. 2. Thoroughly mix the solution in the container holding the contents of the second and third impingers. Pipette a 10-ml aliquot of sample into a 250-ml Erlenmeyer flask. Add 40 ml of isopropanol, 2 to 4 drops of thion indicator, and titrate to a pink endpoint using 0.0100 N barium perchlorate. Repeat the titration with a second aliquot of sample and average the titration values. Replicate titrations must agree within 1 percent or 0.2 ml, whichever is greater.

4.3.3 Blanks. Prepare blanks by adding 2 to 4 drops of thion indicator to 100 ml of 80 percent isopropanol. Titrate the blanks in the same manner as the samples.

5. Calibration.

5.1 Calibrate equipment using the procedures specified in the following sections of Method 5: Section 5.3 (metering system); Section 5.5 (temperature gauges); Section 5.7 (barometer). Note that the recommended leak-check of the metering system, described in Section 5.6 of Method 5, also applies to this method.

5.2 Standardize the barium perchlorate solution with 25 ml of standard sulfuric acid, to which 100 ml of 100 percent isopropanol has been added.

6. Calculations

NOTE: Carry out calculations retaining at least one extra decimal figure beyond that of the acquired data. Round off figures after final calculation.

6.1 Nomenclature.

A_s = Cross-sectional area of nozzle, m² (ft²).

B_w = Water vapor in the gas stream, proportion by volume.

$C_{H_2SO_4}$ = Sulfuric acid (including SO₃) concentration, g/dscm (lb/dscf).

C_{SO_2} = Sulfur dioxide concentration, g/dscm (lb/dscf).

I = Percent of isokinetic sampling.

N = Normality of barium perchlorate titrant, meq/ml.

P_a = Barometric pressure at the sampling site, mm Hg (in. Hg).

P_s = Absolute stack gas pressure, mm Hg (in. Hg).

P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).

T_a = Average absolute dry gas meter temperature (see Figure 8-2), °K (°R).

T_s = Average absolute stack gas temperature (see Figure 8-2), °K (°R).

T_{std} = Standard absolute temperature, 293° K (528° R).

V_s = Volume of sample aliquot titrated, 100 ml for H₂SO₄ and 10 ml for SO₃.

V_{ic} = Total volume of liquid collected in impingers and silica gel, ml.

V_m = Volume of gas sample as measured by dry gas meter, dcm (dcf).

$V_{m, std}$ = Volume of gas sample measured by the dry gas meter corrected to standard conditions, dscm (dscf).

v_s = Average stack gas velocity, calculated by Method 2, Equation 2-9, using data obtained from method 8, m/sec (ft/sec).

V_{sol} = Total volume of solution in which the sulfuric acid or sulfur dioxide sample is contained, 250 ml or 1,000 ml, respectively.

V_t = Volume of barium perchlorate titrant used for the sample, ml.

V_b = Volume of barium perchlorate titrant used for the blank, ml.

Y = Dry gas meter calibration factor.

ΔH = Average pressure drop across orifice meter, mm (in.) H₂O.

θ = Total sampling time, min.

13.6 = Specific gravity of mercury.

60 = sec/min.

100 = Conversion to percent.

6.2 Average dry gas meter temperature and average orifice pressure drop. See data sheet (Figure 8-2).

6.3 Dry Gas Volume. Correct the sample volume measured by the dry gas meter to standard conditions (20° C and 760 mm Hg or 68° F and 29.92 in. Hg) by using Equation 8-1.

$$V_{m(std)} = V_m Y \left(\frac{T_{std}}{T_m} \right) \frac{P_{bar} + \left(\frac{\Delta H}{13.6} \right)}{P_{std}}$$

$$= K_1 V_m Y \frac{P_{bar} + (\Delta H/13.6)}{T_m}$$

Equation 8-1

where:

$K_1 = 0.3858$ °K/mm Hg for metric units.
 $= 17.64$ °R/in. Hg for English units.

Note: If the leak rate observed during any mandatory leak-checks exceeds the specified acceptable rate, the tester shall either correct the value of V_m in Equation 8-1 (as

described in Section 6.3 of Method 5), or shall invalidate the test run.

6.4 Volume of Water Vapor and Moisture Content. Calculate the volume of water vapor using Equation 5-2 of Method 5; the weight of water collected in the impingers and silica gel can be directly converted to milliliters (the specific gravity of water is 1 g/ml). Calculate the moisture content of the stack gas, using Equation 5-3 of Method 5. The "Note" in Section 6.3 of Method 5 also applies to this method. Note that if the effluent gas stream can be considered dry, the volume of water vapor and moisture content need not be calculated.

6.5 Sulfuric acid mist (including SO_3) concentration.

$$C_{H_2SO_4} = K_2 \frac{N(V_i - V_{is}) \left(\frac{V_{std}}{V_s} \right)}{V_{m(std)}}$$

Equation 8-2

where:

$K_2 = 0.04904$ g/milliequivalent for metric units.

$= 1.081 \times 10^{-4}$ lb/meq for English units.

6.6 Sulfur dioxide concentration.

$$C_{SO_2} = K_3 \frac{N(V_i - V_{is}) \left(\frac{V_{std}}{V_s} \right)}{V_{m(std)}}$$

Equation 8-3

where:

$K_3 = 0.03203$ g/meq for metric units.

$= 7.061 \times 10^{-4}$ lb/meq for English units.

6.7 Isokinetic Variation.

6.7.1 Calculation from raw data.

$$I = \frac{V_m Y}{100 T_m [K_1 V_m + \left(\frac{\Delta H}{T_m} \right) P_{bar} + \Delta H/13.6]}$$

$$= \frac{600 V_m P_{bar}}{100 T_m [K_1 V_m + \left(\frac{\Delta H}{T_m} \right) P_{bar} + \Delta H/13.6]}$$

Equation 8-4

where:

$K_1 = 0.003484$ mm Hg-m³/ml·°K for metric units.

$= 0.002876$ in. Hg-ft³/ml·°R for English units.

6.7.2 Calculation from intermediate values.

$$I = \frac{T_m V_{m(std)} P_{std} 100}{T_{std} V_s A_s P_{std} 60 (1 - B_{ws})}$$

$$= K_4 \frac{T_m V_{m(std)}}{P_{std} V_s A_s \theta (1 - B_{ws})}$$

Equation 8-5

where:

$K_4 = 4.320$ for metric units.

$= 0.09450$ for English units.

6.8 Acceptable Results. If 90 percent < I < 110 percent, the results are acceptable. If the results are low in comparison to the standards and I is beyond the acceptable range, the Administrator may opt to accept the results. Use Citation 4 in the Bibliography of Method 5 to make judgments. Otherwise, reject the results and repeat the test.

6.9 Stack Gas Velocity and Volumetric Flow Rate. Calculate the average stack gas velocity and volumetric flow rate, if needed, using data obtained in this method and the equations in Sections 5.2 and 5.3 of Method 2.

7. Bibliography

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METHOD 0010

Modified Method 5
Sampling Train

METHOD 0010

MODIFIED METHOD 5 SAMPLING TRAIN

1.0 SCOPE AND APPLICATION

1.1 This method is applicable to the determination of Destruction and Removal Efficiency (DRE) of semivolatile Principal Organic Hazardous Compounds (POHCs) from incineration systems (PHS, 1967). This method also may be used to determine particulate emission rates from stationary sources as per EPA Method 5 (see References at end of this method).

2.0 SUMMARY OF METHOD

2.1 Gaseous and particulate pollutants are withdrawn from an emission source at an isokinetic sampling rate and are collected in a multicomponent sampling train. Principal components of the train include a high-efficiency glass- or quartz-fiber filter and a packed bed of porous polymeric adsorbent resin. The filter is used to collect organic-laden particulate materials and the porous polymeric resin to adsorb semivolatile organic species. Semivolatile species are defined as compounds with boiling points $>100^{\circ}\text{C}$.

2.2 Comprehensive chemical analyses of the collected sample are conducted to determine the concentration and identity of the organic materials.

3.0 INTERFERENCES

3.1 Oxides of nitrogen (NO_x) are possible interferences in the determination of certain water-soluble compounds such as dioxane, phenol, and urethane; reaction of these compounds with NO_x in the presence of moisture will reduce their concentration. Other possibilities that could result in positive or negative bias are (1) stability of the compounds in methylene chloride, (2) the formation of water-soluble organic salts on the resin in the presence of moisture, and (3) the solvent extraction efficiency of water-soluble compounds from aqueous media. Use of two or more ions per compound for qualitative and quantitative analysis can overcome interference at one mass. These concerns should be addressed on a compound-by-compound basis before using this method.

4.0 APPARATUS AND MATERIALS

4.1 Sampling train:

4.1.1 A schematic of the sampling train used in this method is shown in Figure 1. This sampling train configuration is adapted from EPA Method 5 procedures, and, as such, the majority of the required equipment

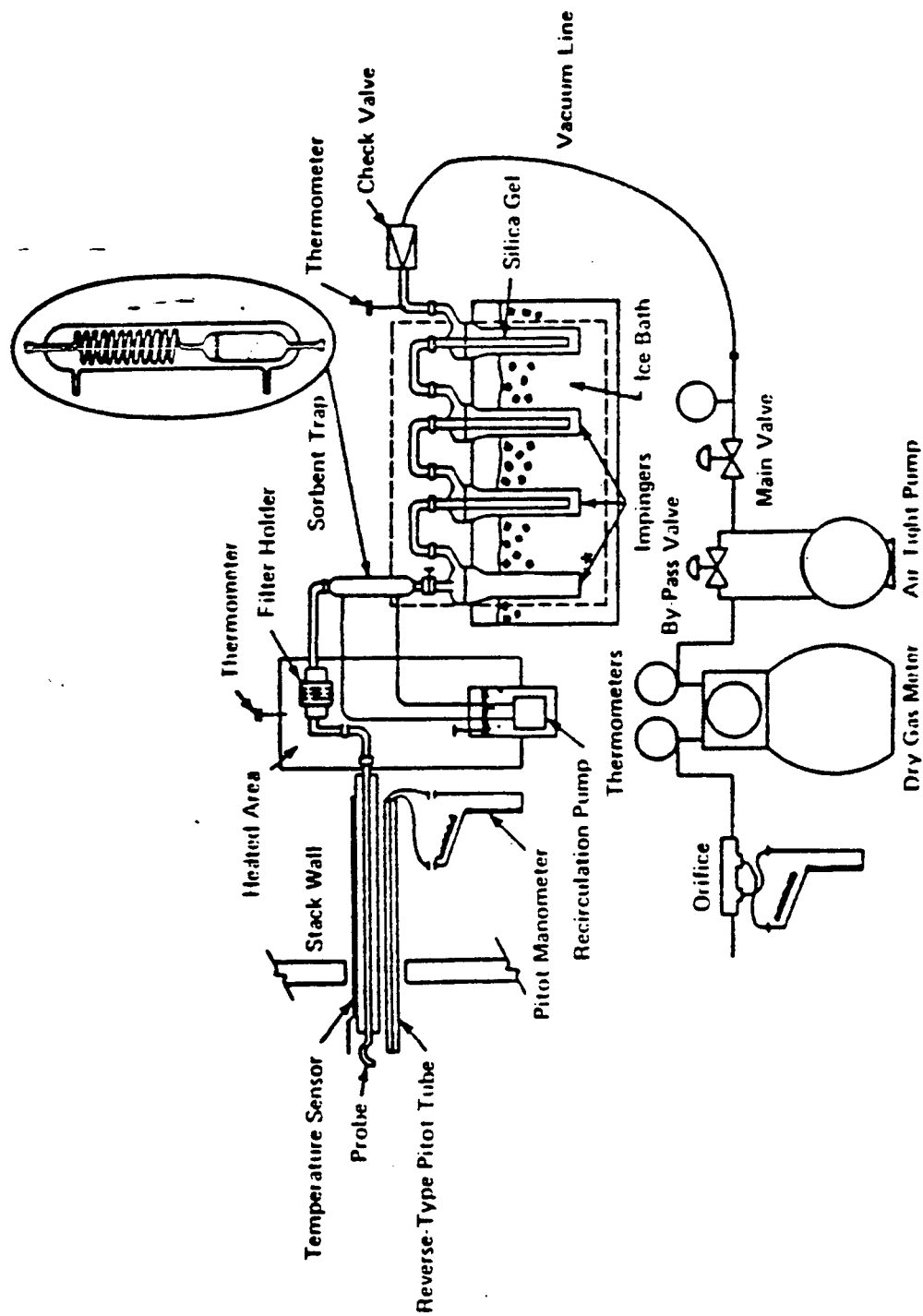


Figure 1. Modified Method 5 Sampling Train.

is identical to that used in EPA Method 5 determinations. The new components required are a condenser coil and a sorbent module, which are used to collect semivolatile organic materials that pass through the glass- or quartz-fiber filter in the gas phase.

4.1.2 Construction details for the basic train components are given in APTD-0581 (see Martin, 1971, in Section 13.0, References); commercial models of this equipment are also available. Specifications for the sorbent module are provided in the following subsections. Additionally, the following subsections list changes to APTD-0581 and identify allowable train configuration modifications.

4.1.3 Basic operating and maintenance procedures for the sampling train are described in APTD-0576 (see Rom, 1972, in Section 13.0, References). As correct usage is important in obtaining valid results, all users should refer to APTD-0576 and adopt the operating and maintenance procedures outlined therein unless otherwise specified. The sampling train consists of the components detailed below.

4.1.3.1 Probe nozzle: Stainless steel (316) or glass with sharp, tapered (30° angle) leading edge. The taper shall be on the outside to preserve a constant I.D. The nozzle shall be buttonhook or elbow design and constructed from seamless tubing (if made of stainless steel). Other construction materials may be considered for particular applications. A range of nozzle sizes suitable for isokinetic sampling should be available in increments of 0.16 cm (1/16 in.), e.g., 0.32-1.27 cm (1/8-1/2 in.), or larger if higher volume sampling trains are used. Each nozzle shall be calibrated according to the procedures outlined in Paragraph 9.1.

4.1.3.2 Probe liner: Borosilicate or quartz-glass tubing with a heating system capable of maintaining a gas temperature of $120 \pm 14^{\circ}\text{C}$ ($248 \pm 25^{\circ}\text{F}$) at the exit end during sampling. (The tester may opt to operate the equipment at a temperature lower than that specified.) Because the actual temperature at the outlet of the probe is not usually monitored during sampling, probes constructed according to APTD-0581 and utilizing the calibration curves of APTD-0576 (or calibrated according to the procedure outlined in APTD-0576) are considered acceptable. Either borosilicate or quartz-glass probe liners may be used for stack temperatures up to about 480°C (900°F). Quartz liners shall be used for temperatures between 480 and 900°C (900 and 1650°F). (The softening temperature for borosilicate is 820°C (1508°F), and for quartz 1500°C (2732°F).) Water-cooling of the stainless steel sheath will be necessary at temperatures approaching and exceeding 500°C .

4.1.3.3 Pitot tube: Type S, as described in Section 2.1 of EPA Method 2, or other appropriate devices (Vollaro, 1976). The pitot tube shall be attached to the probe to allow constant monitoring of the stack-gas velocity. The impact (high-pressure) opening plane of the pitot tube shall be even with or above the nozzle entry plane (see EPA Method 2, Figure 2-6b) during sampling. The Type S pitot tube assembly shall have a known coefficient, determined as outlined in Section 4 of EPA Method 2.

4.1.3.4 Differential pressure gauge: Inclined manometer or equivalent device as described in Section 2.2 of EPA Method 2. One manometer shall be used for velocity-head (ΔP) readings and the other for orifice differential pressure (ΔH) readings.

4.1.3.5 Filter holder: Borosilicate glass, with a glass frit filter support and a sealing gasket. The sealing gasket should be made of materials that will not introduce organic material into the gas stream at the temperature at which the filter holder will be maintained. The gasket shall be constructed of Teflon or materials of equal or better characteristics. The holder design shall provide a positive seal against leakage at any point along the filter circumference. The holder shall be attached immediately to the outlet of the cyclone or cyclone bypass.

4.1.3.6 Filter heating system: Any heating system capable of maintaining a temperature of $120 \pm 14^{\circ}\text{C}$ ($248 \pm 25^{\circ}\text{F}$) around the filter holder during sampling. Other temperatures may be appropriate for particular applications. Alternatively, the tester may opt to operate the equipment at temperatures other than that specified. A temperature gauge capable of measuring temperature to within 3°C (5.4°F) shall be installed so that the temperature around the filter holder can be regulated and monitored during sampling. Heating systems other than the one shown in APTD-0581 may be used.

4.1.3.7 Organic sampling module: This unit consists of three sections, including a gas-conditioning section, a sorbent trap, and a condensate knockout trap. The gas-conditioning system shall be capable of conditioning the gas leaving the back half of the filter holder to a temperature not exceeding 20°C (68°F). The sorbent trap shall be sized to contain approximately 20 g of porous polymeric resin (Rohm and Haas XAD-2 or equivalent) and shall be jacketed to maintain the internal gas temperature at $17 \pm 3^{\circ}\text{C}$ ($62.5 \pm 5.4^{\circ}\text{F}$). The most commonly used coolant is ice water from the impinger ice-water bath, constantly circulated through the outer jacket, using rubber or plastic tubing and a peristaltic pump. The sorbent trap should be outfitted with a glass well or depression, appropriately sized to accommodate a small thermocouple in the trap for monitoring the gas entry temperature. The condensate knockout trap shall be of sufficient size to collect the condensate following gas conditioning. The organic module components shall be oriented to direct the flow of condensate formed vertically downward from the conditioning section, through the adsorbent media, and into the condensate knockout trap. The knockout trap is usually similar in appearance to an empty impinger directly underneath the sorbent module; it may be oversized but should have a shortened center stem (at a minimum, one-half the length of the normal impinger stems) to collect a large volume of condensate without bubbling and overflowing into the impinger train. All surfaces of the organic module wetted by the gas sample shall be fabricated of borosilicate glass, Teflon, or other inert materials. Commercial versions of the

complete organic module are not currently available, but may be assembled from commercially available laboratory glassware and a custom-fabricated sorbent trap. Details of two acceptable designs are shown in Figures 2 and 3 (the thermocouple well is shown in Figure 2).

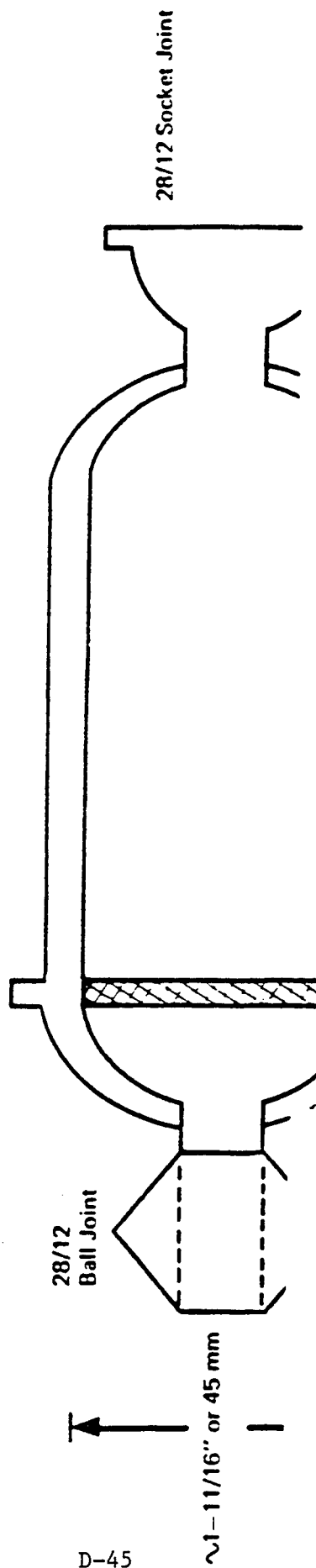
4.1.3.8 Impinger train: To determine the stack-gas moisture content, four 500-mL impingers, connected in series with leak-free ground-glass joints, follow the knockout trap. The first, third, and fourth impingers shall be of the Greenburg-Smith design, modified by replacing the tip with a 1.3-cm (1/2-in.) I.D. glass tube extending about 1.3 cm (1/2 in.) from the bottom of the outer cylinder. The second impinger shall be of the Greenburg-Smith design with the standard tip. The first and second impingers shall contain known quantities of water or appropriate trapping solution. The third shall be empty or charged with a caustic solution, should the stack gas contain hydrochloric acid (HCl). The fourth shall contain a known weight of silica gel or equivalent desiccant.

4.1.3.9 Metering system: The necessary components are a vacuum gauge, leak-free pump, thermometers capable of measuring temperature to within 3°C (5.4°F), dry-gas meter capable of measuring volume to within 1%, and related equipment, as shown in Figure 1. At a minimum, the pump should be capable of 4 cfm free flow, and the dry-gas meter should have a recording capacity of 0-999.9 cu ft with a resolution of 0.005 cu ft. Other metering systems capable of maintaining sampling rates within 10% of isokineticity and of determining sample volumes to within 2% may be used. The metering system must be used in conjunction with a pitot tube to enable checks of isokinetic sampling rates. Sampling trains using metering systems designed for flow rates higher than those described in APTD-0581 and APTD-0576 may be used, provided that the specifications of this method are met.

4.1.3.10 Barometer: Mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 2.5 mm Hg (0.1 in. Hg). In many cases the barometric reading may be obtained from a nearby National Weather Service station, in which case the station value (which is the absolute barometric pressure) is requested and an adjustment for elevation differences between the weather station and sampling point is applied at a rate of minus 2.5 mm Hg (0.1 in. Hg) per 30-m (100 ft) elevation increase (vice versa for elevation decrease).

4.1.3.11 Gas density determination equipment: Temperature sensor and pressure gauge (as described in Sections 2.3 and 2.4 of EPA Method 2), and gas analyzer, if necessary (as described in EPA Method 3). The temperature sensor ideally should be permanently attached to the pitot tube or sampling probe in a fixed configuration such that the tip of the sensor extends beyond the leading edge of the probe sheath and does not touch any metal.

~6.5 in.
or
168 mm



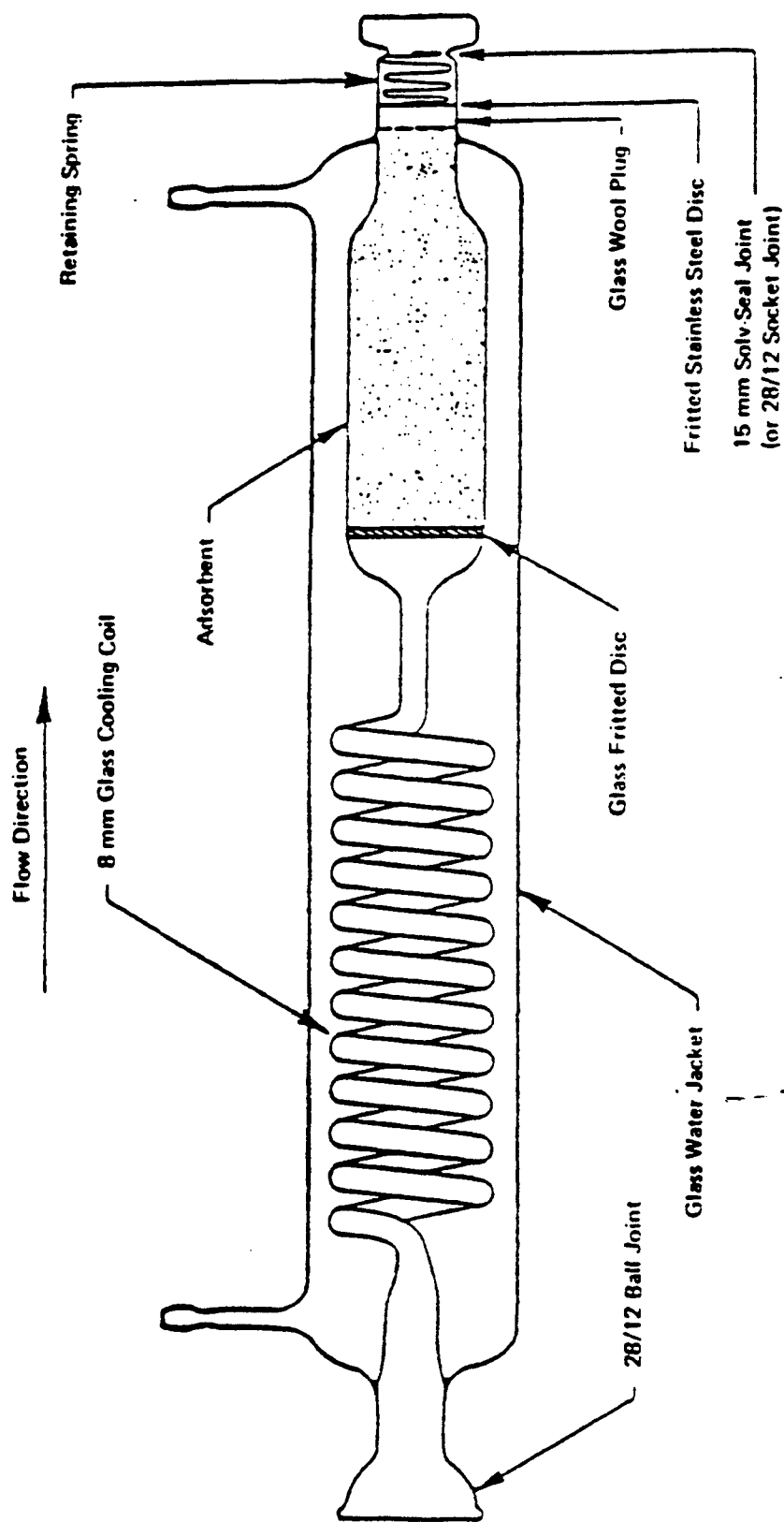


Figure 3. Adsorbent Sampling System.

Alternatively, the sensor may be attached just prior to use in the field. Note, however, that if the temperature sensor is attached in the field, the sensor must be placed in an interference-free arrangement with respect to the Type S pitot tube openings (see EPA Method 2, Figure 2-7). As a second alternative, if a difference of no more than 1% in the average velocity measurement is to be introduced, the temperature gauge need not be attached to the probe or pitot tube.

4.1.3.12 Calibration/field-preparation record: A permanently bound laboratory notebook, in which duplicate copies of data may be made as they are being recorded, is required for documenting and recording calibrations and preparation procedures (i.e., filter and silica gel tare weights, clean XAD-2, quality assurance/quality control check results, dry-gas meter, and thermocouple calibrations, etc.). The duplicate copies should be detachable and should be stored separately in the test program archives.

4.2 Sample Recovery:

4.2.1 Probe liner: Probe nozzle and organic module conditioning section brushes; nylon bristle brushes with stainless steel wire handles are required. The probe brush shall have extensions of stainless steel, Teflon, or inert material at least as long as the probe. The brushes shall be properly sized and shaped to brush out the probe liner, the probe nozzle, and the organic module conditioning section.

4.2.2 Wash bottles: Three. Teflon or glass wash bottles are recommended; polyethylene wash bottles should not be used because organic contaminants may be extracted by exposure to organic solvents used for sample recovery.

4.2.3 Glass sample storage containers: Chemically resistant, borosilicate amber and clear glass bottles, 500-mL or 1,000-mL. Bottles should be tinted to prevent action of light on sample. Screw-cap liners shall be either Teflon or constructed so as to be leak-free and resistant to chemical attack by organic recovery solvents. Narrow-mouth glass bottles have been found to exhibit less tendency toward leakage.

4.2.4 Petri dishes: Glass, sealed around the circumference with wide (1-in.) Teflon tape, for storage and transport of filter samples.

4.2.5 Graduated cylinder and/or balances: To measure condensed water to the nearest 1 mL or 1 g. Graduated cylinders shall have subdivisions not >2 mL. Laboratory triple-beam balances capable of weighing to ± 0.5 g or better are required.

4.2.6 Plastic storage containers: Screw-cap polypropylene or polyethylene containers to store silica gel.

4.2.7 Funnel and rubber policeman: To aid in transfer of silica gel to container (not necessary if silica gel is weighed in field).

4.2.8 Funnels: Glass, to aid in sample recovery.

4.3 Filters: Glass- or quartz-fiber filters, without organic binder, exhibiting at least 99.95% efficiency ($<0.05\%$ penetration) on 0.3- μ m dioctyl phthalate smoke particles. The filter efficiency test shall be conducted in accordance with ASTM standard method D2986-71. Test data from the supplier's quality control program are sufficient for this purpose. In sources containing SO_2 or SO_3 , the filter material must be of a type that is unreactive to SO_2 or SO_3 . Reeve Angel 934 AH or Schleicher and Schuell #3 filters work well under these conditions.

4.4 Crushed ice: Quantities ranging from 10-50 lb may be necessary during a sampling run, depending on ambient air temperature.

4.5 Stopcock grease: Solvent-insoluble, heat-stable silicone grease. Use of silicone grease upstream of the module is not permitted, and amounts used on components located downstream of the organic module shall be minimized. Silicone grease usage is not necessary if screw-on connectors and Teflon sleeves or ground-glass joints are used.

4.6 Glass wool: Used to plug the unfritted end of the sorbent module. The glass-wool fiber should be solvent-extracted with methylene chloride in a Soxhlet extractor for 12 hr and air-dried prior to use.

5.0 REAGENTS

5.1 Adsorbent resin: Porous polymeric resin (XAD-2 or equivalent) is recommended. These resins shall be cleaned prior to their use for sample collection. Appendix A of this method should be consulted to determine appropriate precleaning procedure. For best results, resin used should not exhibit a blank of higher than 4 mg/kg of total chromatographable organics (TCO) (see Appendix B) prior to use. Once cleaned, resin should be stored in an airtight, wide-mouth amber glass container with a Teflon-lined cap or placed in one of the glass sorbent modules tightly sealed with Teflon film and elastic bands. The resin should be used within 4 wk of the preparation.

5.2 Silica gel: Indicating type, 6-16 mesh. If previously used, dry at 175°C (350°F) for 2 hr before using. New silica gel may be used as received. Alternatively, other types of desiccants (equivalent or better) may be used, subject to the approval of the Administrator.

5.3 Impinger solutions: Distilled organic-free water (Type II) shall be used, unless sampling is intended to quantify a particular inorganic gaseous species. If sampling is intended to quantify the concentration of additional species, the impinger solution of choice shall be subject to Administrator approval. This water should be prescreened for any compounds of interest. One hundred mL will be added to the specified impinger; the third impinger in the train may be charged with a basic solution (1 N sodium hydroxide or sodium acetate) to protect the sampling pump from acidic gases. Sodium acetate should be used when large sample volumes are anticipated because sodium hydroxide will react with carbon dioxide in aqueous media to form sodium carbonate, which may possibly plug the impinger.

5.4 Sample recovery reagents:

5.4.1 Methylene chloride: Distilled-in-glass grade is required for sample recovery and cleanup (see Note to 5.4.2 below).

5.4.2 Methyl alcohol: Distilled-in-glass grade is required for sample recovery and cleanup.

NOTE: Organic solvents from metal containers may have a high residue blank and should not be used. Sometimes suppliers transfer solvents from metal to glass bottles; thus blanks shall be run prior to field use and only solvents with low blank value ($<0.001\%$) shall be used.

5.4.3 Water: Water (Type II) shall be used for rinsing the organic module and condenser component.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 Because of complexity of this method, field personnel should be trained in and experienced with the test procedures in order to obtain reliable results.

6.2 Laboratory preparation:

6.2.1 All the components shall be maintained and calibrated according to the procedure described in APTD-0576, unless otherwise specified.

6.2.2 Weigh several 200- to 300-g portions of silica gel in airtight containers to the nearest 0.5 g. Record on each container the total weight of the silica gel plus containers. As an alternative to preweighing the silica gel, it may instead be weighed directly in the impinger or sampling holder just prior to train assembly.

6.2.3 Check filters visually against light for irregularities and flaws or pinhole leaks. Label the shipping containers (glass Petri dishes) and keep the filters in these containers at all times except during sampling and weighing.

6.2.4 Desiccate the filters at $20 \pm 5.6^{\circ}\text{C}$ ($68 \pm 10^{\circ}\text{F}$) and ambient pressure for at least 24 hr, and weigh at intervals of at least 6 hr to a constant weight (i.e., $<0.5\text{-mg}$ change from previous weighing), recording results to the nearest 0.1 mg. During each weighing the filter must not be exposed for more than a 2-min period to the laboratory atmosphere and relative humidity above 50%. Alternatively (unless otherwise specified by the Administrator), the filters may be oven-dried at 105°C (220°F) for 2-3 hr, desiccated for 2 hr, and weighed.

6.3 Preliminary field determinations:

6.3.1 Select the sampling site and the minimum number of sampling points according to EPA Method 1 or as specified by the Administrator. Determine the stack pressure, temperature, and range of velocity heads using EPA Method 2. It is recommended that a leak-check of the pitot lines (see EPA Method 2, Section 3.1) be performed. Determine the stack-gas moisture content using EPA Approximation Method 4 or its alternatives to establish estimates of isokinetic sampling-rate settings. Determine the stack-gas dry molecular weight, as described in EPA Method 2, Section 3.6. If integrated EPA Method 3 sampling is used for molecular weight determination, the integrated bag sample shall be taken simultaneously with, and for the same total length of time as, the sample run.

6.3.2 Select a nozzle size based on the range of velocity heads so that it is not necessary to change the nozzle size in order to maintain isokinetic sampling rates. During the run, do not change the nozzle. Ensure that the proper differential pressure gauge is chosen for the range of velocity heads encountered (see Section 2.2 of EPA Method 2).

6.3.3 Select a suitable probe liner and probe length so that all traverse points can be sampled. For large stacks, to reduce the length of the probe, consider sampling from opposite sides of the stack.

6.3.4 A minimum of 3 dscm (105.9 dscf) of sample volume is required for the determination of the Destruction and Removal Efficiency (DRE) of POHCs from incineration systems. Additional sample volume shall be collected as necessitated by analytical detection limit constraints. To determine the minimum sample volume required, refer to sample calculations in Section 10.0.

6.3.5 Determine the total length of sampling time needed to obtain the identified minimum volume by comparing the anticipated average sampling rate with the volume requirement. Allocate the same time to all traverse points defined by EPA Method 1. To avoid timekeeping errors, the length of time sampled at each traverse point should be an integer or an integer plus one-half min.

6.3.6 In some circumstances (e.g., batch cycles) it may be necessary to sample for shorter times at the traverse-points and to obtain smaller gas-sample volumes. In these cases, the Administrator's approval must first be obtained.

6.4 Preparation of collection train:

6.4.1 During preparation and assembly of the sampling train, keep all openings where contamination can occur covered with Teflon film or aluminum foil until just prior to assembly or until sampling is about to begin.

6.4.2 Fill the sorbent trap section of the organic module with approximately 20 g of clean adsorbent resin. While filling, ensure that the trap packs uniformly, to eliminate the possibility of channeling. When freshly cleaned, many adsorbent resins carry a static charge, which will cause clinging to trap walls. This may be minimized by filling the trap in the presence of an antistatic device. Commercial antistatic devices include Model-204 and Model-210 manufactured by the 3M Company, St. Paul, Minnesota.

6.4.3 If an impinger train is used to collect moisture, place 100 mL of water in each of the first two impingers, leave the third impinger empty (or charge with caustic solution, as necessary), and transfer approximately 200-300 g of preweighed silica gel from its container to the fourth impinger. More silica gel may be used, but care should be taken to ensure that it is not entrained and carried out from the impinger during sampling. Place the container in a clean place for later use in the sample recovery. Alternatively, the weight of the silica gel plus impinger may be determined to the nearest 0.5 g and recorded.

6.4.4 Using a tweezer or clean disposable surgical gloves, place a labeled (identified) and weighed filter in the filter holder. Be sure that the filter is properly centered and the gasket properly placed to prevent the sample gas stream from circumventing the filter. Check the filter for tears after assembly is completed.

6.4.5 When glass liners are used, install the selected nozzle using a Viton-A O-ring when stack temperatures are $<260^{\circ}\text{C}$ (500°F) and a woven glass-fiber gasket when temperatures are higher. See APTD-0576 (Rom, 1972) for details. Other connecting systems utilizing either 316 stainless steel or Teflon ferrules may be used. When metal liners are used, install the nozzle as above, or by a leak-free direct mechanical connection. Mark the probe with heat-resistant tape or by some other method to denote the proper distance into the stack or duct for each sampling point.

6.4.6 Set up the train as in Figure 1. During assembly, do not use any silicone grease on ground-glass joints that are located upstream of the organic module. A very light coating of silicone grease may be used on all ground-glass joints that are located downstream of the organic module, but it should be limited to the outer portion (see APTD-0576) of the ground-glass joints to minimize silicone-grease contamination. Subject to the approval of the Administrator, a glass cyclone may be used between the probe and the filter holder when the total particulate catch is expected to exceed 100 mg or when water droplets are present in the stack. The organic module condenser must be maintained at a temperature of $17 \pm 3^{\circ}\text{C}$. Connect all temperature sensors to an appropriate potentiometer/display unit. Check all temperature sensors at ambient temperature.

6.4.7 Place crushed ice around the impingers and the organic module condensate knockout.

6.4.8 Turn on the sorbent module and condenser coil coolant recirculating pump and begin monitoring the sorbent module gas entry temperature. Ensure proper sorbent module gas entry temperature before proceeding and again before any sampling is initiated. It is extremely important that the XAD-2 resin temperature never exceed 50°C (122°F), because thermal decomposition will occur. During testing, the XAD-2 temperature must not exceed 20°C (68°F) for efficient capture of the semivolatile species of interest.

6.4.9 Turn on and set the filter and probe heating systems at the desired operating temperatures. Allow time for the temperatures to stabilize.

6.5 Leak-check procedures

6.5.1 Pre-test leak-check:

6.5.1.1 Because the number of additional intercomponent connections in the Semi-VOST train (over the M5 Train) increases the possibility of leakage, a pre-test leak-check is required.

6.5.1.2 After the sampling train has been assembled, turn on and set the filter and probe heating systems at the desired operating temperatures. Allow time for the temperatures to stabilize. If a Viton A O-ring or other leak-free connection is used in assembling the probe nozzle to the probe liner, leak-check the train at the sampling site by plugging the nozzle and pulling a 381-mm Hg (15-in. Hg) vacuum.

(NOTE: A lower vacuum may be used, provided that it is not exceeded during the test.)

6.5.1.3 If an asbestos string is used, do not connect the probe to the train during the leak-check. Instead, leak-check the train by first attaching a carbon-filled leak-check impinger (shown in Figure 4) to the inlet of the filter holder (cyclone, if applicable) and then plugging the inlet and pulling a 381-mm Hg (15-in. Hg) vacuum. (Again, a lower vacuum may be used, provided that it is not exceeded during the test.) Then, connect the probe to the train and leak-check at about 25-mm Hg (1-in. Hg) vacuum; alternatively, leak-check the probe with the rest of the sampling train in one step at 381-mm Hg (15-in. Hg) vacuum. Leakage rates in excess of 4% of the average sampling rate or $>0.00057 \text{ m}^3/\text{min}$ (0.02 cfm), whichever is less, are unacceptable.

6.5.1.4 The following leak-check instructions for the sampling train described in APTD-0576 and APTD-0581 may be helpful. Start the pump with fine-adjust valve fully open and coarse-adjust valve completely closed. Partially open the coarse-adjust valve and slowly close the fine-adjust valve until the desired vacuum is reached. Do not reverse direction of the fine-adjust valve; this will cause water to back up into the organic module. If the desired vacuum is exceeded, either leak-check at this higher vacuum or end the leak-check, as shown below, and start over.

CROSS SECTIONAL VIEW
Leak Testing Apparatus

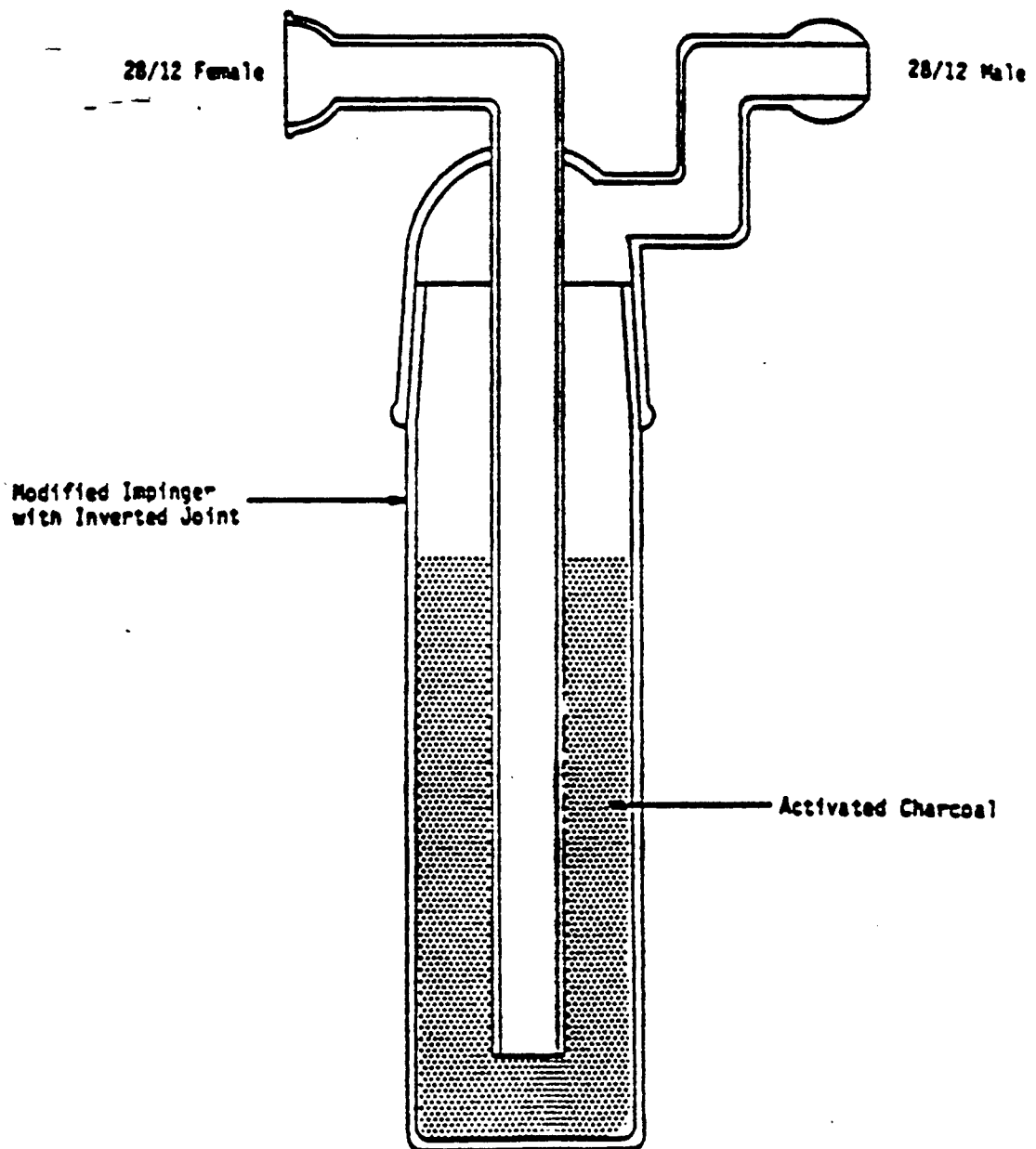


Figure 4. Leak-check impinger.

6.5.1.5 When the leak-check is completed, first slowly remove the plug from the inlet to the probe, filter holder, or cyclone (if applicable). When the vacuum drops to 127 mm (5 in.) Hg or less, immediately close the coarse-adjust valve. Switch off the pumping system and reopen the fine-adjust valve. Do not reopen the fine-adjust valve until the coarse-adjust valve has been closed. This prevents the water in the impingers from being forced backward into the organic module and silica gel from being entrained backward into the third impinger.

6.5.2 Leak-checks during sampling run:

6.5.2.1 If, during the sampling run, a component (e.g., filter assembly, impinger, or sorbent trap) change becomes necessary, a leak-check shall be conducted immediately after the interruption of sampling and before the change is made. The leak-check shall be done according to the procedure outlined in Paragraph 6.5.1, except that it shall be done at a vacuum greater than or equal to the maximum value recorded up to that point in the test. If the leakage rate is found to be no greater than $0.00057 \text{ m}^3/\text{min}$ (0.02 cfm) or 4% of the average sampling rate (whichever is less), the results are acceptable, and no correction will need to be applied to the total volume of dry gas metered. If a higher leakage rate is obtained, the tester shall void the sampling run. (It should be noted that any "correction" of the sample volume by calculation by calculation reduces the integrity of the pollutant concentrations data generated and must be avoided.)

6.5.2.2 Immediately after a component change, and before sampling is reinitiated, a leak-check similar to a pre-test leak-check must also be conducted.

6.5.3 Post-test leak-check:

6.5.3.1 A leak-check is mandatory at the conclusion of each sampling run. The leak-check shall be done with the same procedures as those with the pre-test leak-check, except that it shall be conducted at a vacuum greater than or equal to the maximum value reached during the sampling run. If the leakage rate is found to be no greater than $0.00057 \text{ m}^3/\text{min}$ (0.02 cfm) or 4% of the average sampling rate (whichever is less), the results are acceptable, and no correction need be applied to the total volume of dry gas metered. If, however, a higher leakage rate is obtained, the tester shall either record the leakage rate, correct the sample volume (as shown in the calculation section of this method), and consider the data obtained of questionable reliability, or void the sampling run.

6.6 Sampling-train operation:

6.6.1 During the sampling run, maintain an isokinetic sampling rate to within 10% of true isokinetic, unless otherwise specified by the Administrator. Maintain a temperature around the filter of $120 \pm 14^\circ\text{C}$ ($248 \pm 25^\circ\text{F}$) and a gas temperature entering the sorbent trap at a maximum of 20°C (68°F).

6.6.2 For each run, record the data required on a data sheet such as the one shown in Figure 5. Be sure to record the initial dry-gas meter reading. Record the dry-gas meter readings at the beginning and end of each sampling time increment, when changes in flow rates are made before and after each leak-check, and when sampling is halted. Take other readings required by Figure 5 at least once at each sample point during each time increment and additional readings when significant changes (20% variation in velocity-head readings) necessitate additional adjustments in flow rate. Level and zero the manometer. Because the manometer level and zero may drift due to vibrations and temperature changes, make periodic checks during the traverse.

6.6.3 Clean the stack access ports prior to the test run to eliminate the chance of sampling deposited material. To begin sampling, remove the nozzle cap, verify that the filter and probe heating systems are at the specified temperature, and verify that the pitot tube and probe are properly positioned. Position the nozzle at the first traverse point, with the tip pointing directly into the gas stream. Immediately start the pump and adjust the flow to isokinetic conditions. Nomographs, which aid in the rapid adjustment of the isokinetic sampling rate without excessive computations, are available. These nomographs are designed for use when the Type S pitot-tube coefficient is 0.84 ± 0.02 and the stack-gas equivalent density (dry molecular weight) is equal to 29 ± 4 . APTD-0576 details the procedure for using the nomographs. If the stack-gas molecular weight and the pitot-tube coefficient are outside the above ranges, do not use the nomographs unless appropriate steps (Shigehara, 1974) are taken to compensate for the deviations.

6.6.4 When the stack is under significant negative pressure (equivalent to the height of the impinger stem), take care to close the coarse-adjust valve before inserting the probe into the stack, to prevent water from backing into the organic module. If necessary, the pump may be turned on with the coarse-adjust valve closed.

6.6.5 When the probe is in position, block off the openings around the probe and stack access port to prevent unrepresentative dilution of the gas stream.

6.6.6 Traverse the stack cross section, as required by EPA Method 1 or as specified by the Administrator, being careful not to bump the probe nozzle into the stack walls when sampling near the walls or when removing or inserting the probe through the access port, in order to minimize the chance of extracting deposited material.

6.6.7 During the test run, make periodic adjustments to keep the temperature around the filter holder and the organic module at the proper levels; add more ice and, if necessary, salt to maintain a temperature of $<20^{\circ}\text{C}$ (68°F) at the condenser/silica gel outlet. Also, periodically check the level and zero of the manometer.

Pitot Tube Coefficient C_p _____[illegible]

Figure 5. Particulate field data.

6.6.8 If the pressure drop across the filter or sorbent trap becomes too high, making isokinetic sampling difficult to maintain, the filter/sorbent trap may be replaced in the midst of a sample run. Using another complete filter holder/sorbent trap assembly is recommended, rather than attempting to change the filter and resin themselves. After a new filter/sorbent trap assembly is installed, conduct a leak-check. The total particulate weight shall include the summation of all filter assembly catches.

6.6.9 A single train shall be used for the entire sample run, except in cases where simultaneous sampling is required in two or more separate ducts or at two or more different locations within the same duct, or in cases where equipment failure necessitates a change of trains. In all other situations, the use of two or more trains will be subject to the approval of the Administrator.

6.6.10 Note that when two or more trains are used, separate analysis of the front-half (if applicable) organic-module and impinger (if applicable) catches from each train shall be performed, unless identical nozzle sizes were used on all trains. In that case, the front-half catches from the individual trains may be combined (as may the impinger catches), and one analysis of front-half catch and one analysis of impinger catch may be performed.

6.6.11 At the end of the sample run, turn off the coarse-adjust valve, remove the probe and nozzle from the stack, turn off the pump, record the final dry-gas meter reading, and conduct a post-test leak-check. Also, leak-check the pitot lines as described in EPA Method 2. The lines must pass this leak-check in order to validate the velocity-head data.

6.6.12 Calculate percent isokineticity (see Section 10.8) to determine whether the run was valid or another test run should be made.

7.0 SAMPLE RECOVERY

7.1 Preparation:

7.1.1 Proper cleanup procedure begins as soon as the probe is removed from the stack at the end of the sampling period. Allow the probe to cool. When the probe can be safely handled, wipe off all external particulate matter near the tip of the probe nozzle and place a cap over the tip to prevent losing or gaining particulate matter. Do not cap the probe tip tightly while the sampling train is cooling down because this will create a vacuum in the filter holder, drawing water from the impingers into the sorbent module.

7.1.2 Before moving the sample train to the cleanup site, remove the probe from the sample train and cap the open outlet, being careful not to lose any condensate that might be present. Cap the filter inlet.

Remove the umbilical cord from the last impinger and cap the impinger. If a flexible line is used between the organic module and the filter holder, disconnect the line at the filter holder and let any condensed water or liquid drain into the organic module.

7.1.3 Cap the filter-holder outlet and the inlet to the organic module. Separate the sorbent trap section of the organic module from the condensate knockout trap and the gas-conditioning section. Cap all organic module openings. Disconnect the organic-module knockout trap from the impinger train inlet and cap both of these openings. Ground-glass stoppers, Teflon caps, or caps of other inert materials may be used to seal all openings.

7.1.4 Transfer the probe, the filter, the organic-module components, and the impinger/condenser assembly to the cleanup area. This area should be clean and protected from the weather to minimize sample contamination or loss.

7.1.5 Save a portion of all washing solutions (methanol/methylene chloride, Type II water) used for cleanup as a blank. Transfer 200 mL of each solution directly from the wash bottle being used and place each in a separate, prelabeled glass sample container.

7.1.6 Inspect the train prior to and during disassembly and note any abnormal conditions.

7.2 Sample containers:

7.2.1 Container no. 1: Carefully remove the filter from the filter holder and place it in its identified Petri dish container. Use a pair or pairs of tweezers to handle the filter. If it is necessary to fold the filter, ensure that the particulate cake is inside the fold. Carefully transfer to the Petri dish any particulate matter or filter fibers that adhere to the filter-holder gasket, using a dry nylon bristle brush or sharp-edged blade, or both. Label the container and seal with 1-in.-wide Teflon tape around the circumference of the lid.

7.2.2 Container no. 2: Taking care that dust on the outside of the probe or other exterior surfaces does not get into the sample, quantitatively recover particulate matter or any condensate from the probe nozzle, probe fitting, probe liner, and front half of the filter holder by washing these components first with methanol/methylene chloride (1:1 v/v) into a glass container. Distilled water may also be used. Retain a water and solvent blank and analyze in the same manner as with the samples. Perform rinses as follows:

7.2.2.1 Carefully remove the probe nozzle and clean the inside surface by rinsing with the solvent mixture (1:1 v/v methanol/methylene chloride) from a wash bottle and brushing with a nylon bristle brush. Brush until the rinse shows no visible particles; then make a final rinse of the inside surface with the solvent mix. Brush and rinse the inside parts of the Swagelok fitting with the solvent mix in a similar way until no visible particles remain.

7.2.2.2 Have two people rinse the probe liner with the solvent mix by tilting and rotating the probe while squirting solvent into its upper end so that all inside surfaces will be wetted with solvent. Let the solvent drain from the lower end into the sample container. A glass funnel may be used to aid in transferring liquid washes to the container.

7.2.2.3 Follow the solvent rinse with a probe brush. Hold the probe in an inclined position and squirt solvent into the upper end while pushing the probe brush through the probe with a twisting action; place a sample container underneath the lower end of the probe and catch any solvent and particulate matter that is brushed from the probe. Run the brush through the probe three times or more until no visible particulate matter is carried out with the solvent or until none remains in the probe liner on visual inspection. With stainless steel or other metal probes, run the brush through in the above-prescribed manner at least six times (metal probes have small crevices in which particulate matter can be entrapped). Rinse the brush with solvent and quantitatively collect these washings in the sample container. After the brushing, make a final solvent rinse of the probe as described above.

7.2.2.4 It is recommended that two people work together to clean the probe to minimize sample losses. Between sampling runs, keep brushes clean and protected from contamination.

7.2.2.5 Clean the inside of the front half of the filter holder and cyclone/cyclone flask, if used, by rubbing the surfaces with a nylon bristle brush and rinsing with methanol/methylene chloride (1:1 v/v) mixture. Rinse each surface three times or more if needed to remove visible particulate. Make a final rinse of the brush and filter holder. Carefully rinse out the glass cyclone and cyclone flask (if applicable). Brush and rinse any particulate material adhering to the inner surfaces of these components into the front-half rinse sample. After all solvent washings and particulate matter have been collected in the sample container, tighten the lid on the sample container so that solvent will not leak out when it is shipped to the laboratory. Mark the height of the fluid level to determine whether leakage occurs during transport. Label the container to identify its contents.

7.2.3 Container no. 3: The sorbent trap section of the organic module may be used as a sample transport container, or the spent resin may be transferred to a separate glass bottle for shipment. If the sorbent trap itself is used as the transport container, both ends should be sealed with tightly fitting caps or plugs. Ground-glass stoppers or Teflon caps may be used. The sorbent trap should then be labeled, covered with aluminum foil, and packaged on ice for transport to the laboratory. If a separate bottle is used, the spent resin should be quantitatively transferred from the trap into the clean bottle. Resin that adheres to the walls of the trap should be recovered using a rubber policeman or spatula and added to this bottle.

7.2.4 Container no. 4: Measure the volume of condensate collected in the condensate knockout section of the organic module to within ± 1 mL by using a graduated cylinder or by weighing to within ± 0.5 g using a triple-beam balance. Record the volume or weight of liquid present and note any discoloration or film in the liquid catch. Transfer this liquid to a prelabeled glass sample container. Inspect the back half of the filter housing and the gas-conditioning section of the organic module. If condensate is observed, transfer it to a graduated or weighing bottle and measure the volume, as described above. Add this material to the condensate knockout-trap catch.

7.2.5 Container no. 5: All sampling train components located between the high-efficiency glass- or quartz-fiber filter and the first wet impinger or the final condenser system (including the heated Teflon line connecting the filter outlet to the condenser) should be thoroughly rinsed with methanol/methylene chloride (1:1 v/v) and the rinsings combined. This rinse shall be separated from the condensate. If the spent resin is transferred from the sorbent trap to a separate sample container for transport, the sorbent trap shall be thoroughly rinsed until all sample-wetted surfaces appear clean. Visible films should be removed by brushing. Whenever train components are brushed, the brush should be subsequently rinsed with solvent mixture and the rinsings added to this container.

7.2.6 Container no. 6: Note the color of the indicating silica gel to determine if it has been completely spent and make a notation of its condition. Transfer the silica gel from the fourth impinger to its original container and seal. A funnel may make it easier to pour the silica gel without spilling. A rubber policeman may be used as an aid in removing the silica gel from the impinger. It is not necessary to remove the small amount of dust particles that may adhere strongly to the impinger wall. Because the gain in weight is to be used for moisture calculations, do not use any water or other liquids to transfer the silica gel. If a balance is available in the field, weigh the container and its contents to 0.5 g or better.

7.3 Impinger water:

7.3.1 Make a notation of any color or film in the liquid catch. Measure the liquid in the first three impingers to within ± 1 mL by using a graduated cylinder or by weighing it to within ± 0.5 g by using a balance (if one is available). Record the volume or weight of liquid present. This information is required to calculate the moisture content of the effluent gas.

7.3.2 Discard the liquid after measuring and recording the volume or weight, unless analysis of the impinger catch is required (see Paragraph 4.1.3.7). Amber glass containers should be used for storage of impinger catch, if required.

7.3.3 If a different type of condenser is used, measure the amount of moisture condensed either volumetrically or gravimetrically.

7.4 Sample preparation for shipment: Prior to shipment, recheck all sample containers to ensure that the caps are well secured. Seal the lids of all containers around the circumference with Teflon tape. Ship all liquid samples upright on ice and all particulate filters with the particulate catch facing upward. The particulate filters should be shipped unrefrigerated.

8.0 ANALYSIS

8.1 Sample preparation:

8.1.1 General: The preparation steps for all samples will result in a finite volume of concentrated solvent. The final sample volume (usually in the 1- to 10-mL range) is then subjected to analysis by GC/MS. All samples should be inspected and the appearance documented. All samples are to be spiked with surrogate standards as received from the field prior to any sample manipulations. The spike should be at a level equivalent to 10 times the MDL when the solvent is reduced in volume to the desired level (i.e., 10 mL). The spiking compounds should be the stable isotopically labeled analog of the compounds of interest or a compound that would exhibit properties similar to the compounds of interest, be easily chromatographed, and not interfere with the analysis of the compounds of interest. Suggested surrogate spiking compounds are: deuterated naphthalene, chrysene, phenol, nitrobenzene, chlorobenzene, toluene, and carbon-13-labeled pentachlorophenol.

8.1.2 Condensate: The "condensate" is the moisture collected in the first impinger following the XAD-2 module. Spike the condensate with the surrogate standards. The volume is measured and recorded and then transferred to a separatory funnel. The pH is to be adjusted to pH 2 with 6 N sulfuric acid, if necessary. The sample container and graduated cylinder are sequentially rinsed with three successive 10-mL aliquots of the extraction solvent and added to the separatory funnel. The ratio of solvent to aqueous sample should be maintained at 1:3. Extract the sample by vigorously shaking the separatory funnel for 5 min. After complete separation of the phases, remove the solvent and transfer to a Kuderna-Danish concentrator (K-D), filtering through a bed of precleaned, dry sodium sulfate. Repeat the extraction step two additional times. Adjust the pH to 11 with 6 N sodium hydroxide and reextract combining the acid and base extracts. Rinse the sodium sulfate into the K-D with fresh solvent and discard the desiccant. Add Teflon boiling chips and concentrate to 10 mL by reducing the volume to slightly less than 10 mL and then bringing to volume with fresh solvent. In order to achieve the necessary detection limit, the sample volume can be further reduced to 1 mL by using a micro column K-D or nitrogen blow-down. Should the sample start to exhibit precipitation, the concentration step should be stopped and the sample redissolved with fresh solvent taking the volume to some finite amount. After adding a standard (for the purpose of quantitation by GC/MS), the sample is ready for analysis, as discussed in Paragraph 8.2.

8.1.3 Impinger: Spike the sample with the surrogate standards; measure and record the volume and transfer to a separatory funnel. Proceed as described in Paragraph 8.1.2.

8.1.4 XAD-2: Spike the resin directly with the surrogate standards. Transfer the resin to the all-glass thimbles by the following procedure (care should be taken so as not to contaminate the thimble by touching it with anything other than tweezers or other solvent-rinsed mechanical holding devices). Suspend the XAD-2 module directly over the thimble. The glass frit of the module (see Figure 2) should be in the up position. The thimble is contained in a clean beaker, which will serve to catch the solvent rinses. Using a Teflon squeeze bottle, flush the XAD-2 into the thimble. Thoroughly rinse the glass module with solvent into the beaker containing the thimble. Add the XAD-2 glass-wool plug to the thimble. Cover the XAD-2 in the thimble with a precleaned glass-wool plug sufficient to prevent the resin from floating into the solvent reservoir of the extractor. If the resin is wet, effective extraction can be accomplished by loosely packing the resin in the thimble. If a question arises concerning the completeness of the extraction, a second extraction, without a spike, is advised. The thimble is placed in the extractor and the rinse solvent contained in the beaker is added to the solvent reservoir. Additional solvent is added to make the reservoir approximately two-thirds full. Add Teflon boiling chips and assemble the apparatus. Adjust the heat source to cause the extractor to cycle 5-6 times per hr. Extract the resin for 16 hr. Transfer the solvent and three 10-mL rinses of the reservoir to a K-D and concentrate as described in Paragraph 8.1.2.

8.1.5 Particulate filter (and cyclone catch): If particulate loading is to be determined, weigh the filter (and cyclone catch, if applicable). The particulate filter (and cyclone catch, if applicable) is transferred to the glass thimble and extracted simultaneously with the XAD-2 resin.

8.1.6 Train solvent rinses: All train rinses (i.e., probe, impinger, filter housing) using the extraction solvent and methanol are returned to the laboratory as a single sample. If the rinses are contained in more than one container, the intended spike is divided equally among the containers proportioned from a single syringe volume. Transfer the rinse to a separatory funnel and add a sufficient amount of organic-free water so that the methylene chloride becomes immiscible and its volume no longer increases with the addition of more water. The extraction and concentration steps are then performed as described in Paragraph 8.1.2.

8.2 Sample analysis:

8.2.1 The primary analytical tool for the measurement of emissions from hazardous waste incinerators is GC/MS using fused-silica capillary GC columns, as described in Method 8270 in Chapter Four of this manual. Because of the nature of GC/MS instrumentation and the cost associated

with sample analysis, prescreening of the sample extracts by gas chromatography/flame ionization detection (GC/FID) or with electron capture (GC/ECD) is encouraged. Information regarding the complexity and concentration level of a sample prior to GC/MS analysis can be of enormous help. This information can be obtained by using either capillary columns or less expensive packed columns. However, the FID screen should be performed with a column similar to that used with the GC/MS. Keep in mind that GC/FID has a slightly lower detection limit than GC/MS and, therefore, that the concentration of the sample can be adjusted either up or down prior to analysis by GC/MS.

8.2.2 The mass spectrometer will be operated in a full scan (40-450) mode for most of the analyses. The range for which data are acquired in a GC/MS run will be sufficiently broad to encompass the major ions, as listed in Chapter Four, Method 8270, for each of the designated POHCs in an incinerator effluent analysis.

8.2.3 For most purposes, electron ionization (EI) spectra will be collected because a majority of the POHCs give reasonable EI spectra. Also, EI spectra are compatible with the NBS Library of Mass Spectra and other mass spectral references, which aid in the identification process for other components in the incinerator process streams.

8.2.4 To clarify some identifications, chemical ionization (CI) spectra using either positive ions or negative ions will be used to elucidate molecular-weight information and simplify the fragmentation patterns of some compounds. In no case, however, should CI spectra alone be used for compound identification. Refer to Chapter Four, Method 8270, for complete descriptions of GC conditions, MS conditions, and quantitative and quantitative identification.

9.0 CALIBRATION

9.1 Probe nozzle: Probe nozzles shall be calibrated before their initial use in the field. Using a micrometer, measure the inside diameter of the nozzle to the nearest 0.025 mm (0.001 in.). Make measurements at three separate places across the diameter and obtain the average of the measurements. The difference between the high and low numbers shall not exceed 0.1 mm (0.004 in.). When nozzles become nicked, dented, or corroded, they shall be reshaped, sharpened, and recalibrated before use. Each nozzle shall be permanently and uniquely identified.

9.2 Pitot tube: The Type S pitot tube assembly shall be calibrated according to the procedure outlined in Section 4 of EPA Method 2, or assigned a nominal coefficient of 0.84 if it is not visibly nicked, dented, or corroded and if it meets design and intercomponent spacing specifications.

9.3 Metering system:

9.3.1 Before its initial use in the field, the metering system shall be calibrated according to the procedure outlined in APTD-0576. Instead of physically adjusting the dry-gas meter dial readings to correspond to the wet-test meter readings, calibration factors may be used to correct the gas meter dial readings mathematically to the proper values. Before calibrating the metering system, it is suggested that a leak-check be conducted. For metering systems having diaphragm pumps, the normal leak-check procedure will not detect leakages within the pump. For these cases the following leak-check procedure is suggested: Make a 10-min calibration run at $0.00057 \text{ m}^3/\text{min}$ (0.02 cfm); at the end of the run, take the difference of the measured wet-test and dry-gas meter volumes and divide the difference by 10 to get the leak rate. The leak rate should not exceed $0.00057 \text{ m}^3/\text{min}$ (0.02 cfm).

9.3.2 After each field use, the calibration of the metering system shall be checked by performing three calibration runs at a single intermediate orifice setting (based on the previous field test). The vacuum shall be set at the maximum value reached during the test series. To adjust the vacuum, insert a valve between the wet-test meter and the inlet of the metering system. Calculate the average value of the calibration factor. If the calibration has changed by more than 5%, recalibrate the meter over the full range of orifice settings, as outlined in APTD-0576.

9.3.3 Leak-check of metering system: That portion of the sampling train from the pump to the orifice meter (see Figure 1) should be leak-checked prior to initial use and after each shipment. Leakage after the pump will result in less volume being recorded than is actually sampled. The following procedure is suggested (see Figure 6): Close the main valve on the meter box. Insert a one-hole rubber stopper with rubber tubing attached into the orifice exhaust pipe. Disconnect and vent the low side of the orifice manometer. Close off the low side orifice tap. Pressurize the system to 13-18 cm (5-7 in.) water column by blowing into the rubber tubing. Pinch off the tubing and observe the manometer for 1 min. A loss of pressure on the manometer indicates a leak in the meter box. Leaks, if present, must be corrected.

NOTE: If the dry-gas-meter coefficient values obtained before and after a test series differ by >5%, either the test series shall be voided or calculations for test series shall be performed using whichever meter coefficient value (i.e., before or after) gives the lower value of total sample volume.

9.4 Probe heater: The probe-heating system shall be calibrated before its initial use in the field according to the procedure outlined in APTD-0576. Probes constructed according to APTD-0581 need not be calibrated if the calibration curves in APTD-0576 are used.

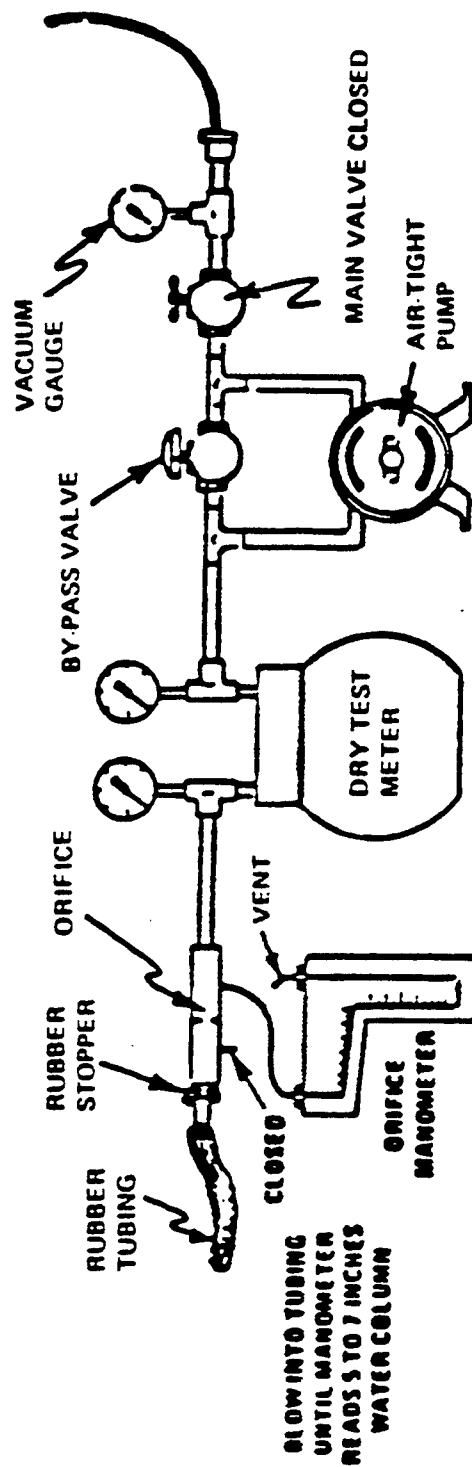


Figure 6. Leak-check of meter box.

9.5 Temperature gauges: Each thermocouple must be permanently and uniquely marked on the casting; all mercury-in-glass reference thermometers must conform to ASTM E-1 63C or 63F specifications. Thermocouples should be calibrated in the laboratory with and without the use of extension leads. If extension leads are used in the field, the thermocouple readings at ambient air temperatures, with and without the extension lead, must be noted and recorded. Correction is necessary if the use of an extension lead produces a change $>1.5\%$.

9.5.1 Impinger, organic module, and dry-gas meter thermocouples: For the thermocouples used to measure the temperature of the gas leaving the impinger train and the XAD-2 resin bed, three-point calibration at ice-water, room-air, and boiling-water temperatures is necessary. Accept the thermocouples only if the readings at all three temperatures agree to $\pm 2^{\circ}\text{C}$ (3.6°F) with those of the absolute value of the reference thermometer.

9.5.2 Probe and stack thermocouple: For the thermocouples used to indicate the probe and stack temperatures, a three-point calibration at ice-water, boiling-water, and hot-oil-bath temperatures must be performed; it is recommended that room-air temperature be added, and that the thermometer and the thermocouple agree to within 1.5% at each of the calibration points. A calibration curve (equation) may be constructed (calculated) and the data extrapolated to cover the entire temperature range suggested by the manufacturer.

9.6 Barometer: Adjust the barometer initially and before each test series to agree to within ± 25 mm Hg (0.1 in. Hg) of the mercury barometer or the corrected barometric pressure value reported by a nearby National Weather Service Station (same altitude above sea level).

9.7 Triple-beam balance: Calibrate the triple-beam balance before each test series, using Class-S standard weights; the weights must be within $\pm 0.5\%$ of the standards, or the balance must be adjusted to meet these limits.

10.0 CALCULATIONS

10.1 Carry out calculations. Round off figures after the final calculation to the correct number of significant figures. _ _ _

10.2 Nomenclature:

A_n = Cross-sectional area of nozzle, m^2 (ft^2).

B_{ws} = Water vapor in the gas stream, proportion by volume.

C_d = Type S pitot tube coefficient (nominally 0.84 ± 0.02), dimensionless.

I = Percent of isokinetic sampling.

- L_a = Maximum acceptable leakage rate for a leak-check, either pre-test or following a component change; equal to $0.00057 \text{ m}^3/\text{min}$ (0.02 cfm) or 4% of the average sampling rate, whichever is less.
- L_i = Individual leakage rate observed during the leak-check conducted prior to the "ith" component change ($i = 1, 2, 3 \dots n$) m^3/min (cfm).
- L_p = Leakage rate observed during the post-test leak-check, m^3/min (cfm).
- M_d = Stack-gas dry molecular weight, g/g-mole (lb/lb-mole).
- M_w = Molecular weight of water, 18.0 g/g-mole (18.0 lb/lb-mole).
- P_{bar} = Barometric pressure at the sampling site, mm Hg (in. Hg).
- P_s = Absolute stack-gas pressure, mm Hg (in. Hg).
- P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).
- R = Ideal gas constant, $0.06236 \text{ mm Hg} \cdot \text{m}^3/\text{K} \cdot \text{g-mole}$ ($21.85 \text{ in. Hg} \cdot \text{ft}^3/^\circ\text{R} \cdot \text{lb-mole}$).
- T_m = Absolute average dry-gas meter temperature (see Figure 6), K ($^\circ\text{R}$).
- T_s = Absolute average stack-gas temperature (see Figure 6), K ($^\circ\text{R}$).
- T_{std} = Standard absolute temperature, 293K (528°R).
- V_{lc} = Total volume of liquid collected in the organic module condensate knockout trap, the impingers, and silica gel, mL.
- V_m = Volume of gas sample as measured by dry-gas meter, dscm (dscf).
- $V_m(\text{std})$ = Volume of gas sample measured by the dry-gas meter, corrected to standard conditions, dscm (dscf).
- $V_w(\text{std})$ = Volume of water vapor in the gas sample, corrected to standard conditions, scm (scf).
- V_s = Stack-gas velocity, calculated by Method 2, Equation 2-9, using data obtained from Method 5, m/sec (ft/sec).
- W_a = Weight of residue in acetone wash, mg.
- γ = Dry-gas-meter calibration factor, dimensionless.
- ΔH = Average pressure differential across the orifice meter (see Figure 2), mm H₂O (in. H₂O).

ρ_w = Density of water, 0.9982 g/mL (0.002201 lb/mL).

θ = Total sampling time, min.

θ_1 = Sampling time interval from the beginning of a run until the first component change, min.

θ_i = Sampling time interval between two successive component changes, beginning with the interval between the first and second changes, min.

θ_p = Sampling time interval from the final (n^{th}) component change until the end of the sampling run, min.

13.6 = Specific gravity of mercury.

60 = sec/min.

100 = Conversion to percent.

10.3 Average dry-gas-meter temperature and average orifice pressure drop: See data sheet (Figure 5, above).

10.4 Dry-gas volume: Correct the sample measured by the dry-gas meter to standard conditions (20°C, 760 mm Hg [68°F, 29.92 in. Hg]) by using Equation 1:

$$V_{m(\text{std})} = V_m \gamma \frac{T_{\text{std}}}{T_m} \frac{P_{\text{bar}} + \Delta H/13.6}{P_{\text{std}}} = K_1 V_m \gamma \frac{P_{\text{bar}} + \Delta H/13.6}{T_m} \quad (1)$$

where:

K_1 = 0.3858 K/mm Hg for metric units, or
 K_1 = 17.64°R/in. Hg for English units.

It should be noted that Equation 1 can be used as written, unless the leakage rate observed during any of the mandatory leak-checks (i.e., the post-test leak-check or leak-checks conducted prior to component changes) exceeds L_a . If L_p or L_i exceeds L_a , Equation 1 must be modified as follows:

- a. Case I (no component changes made during sampling run): Replace V_m in Equation 1 with the expression:

$$V_m - (L_p - L_a)$$

- b. Case II (one or more component changes made during the sampling run): Replace V_m in Equation 1 by the expression:

$$V_m = (L_1 - L_a)\theta_1 - \sum_{i=2}^n (L_i - L_a)\theta_i - (L_p - L_a)\theta_p$$

and substitute only for those leakage rates (L_1 or L_p) that exceed L_a .

10.5 Volume of water vapor:

$$V_{w(std)} = \bar{V}_{1c} \cdot \frac{P_w}{M_w} \cdot \frac{RT_{std}}{P_{std}} = K_2 V_{1c} \quad (2)$$

where:

$K_2 = 0.001333 \text{ m}^3/\text{mL}$ for metric units, or
 $K_2 = 0.04707 \text{ ft}^3/\text{mL}$ for English units.

10.6 Moisture content:

$$B_{ws} = \frac{V_{w(std)}}{V_{m(std)} + V_{w(std)}} \quad (3)$$

NOTE: In saturated or water-droplet-laden gas streams, two calculations of the moisture content of the stack gas shall be made, one from the impinger analysis (Equation 3) and a second from the assumption of saturated conditions. The lower of the two values of B_w shall be considered correct. The procedure for determining the moisture content based upon assumption of saturated conditions is given in the Note to Section 1.2 of Method 4. For the purposes of this method, the average stack-gas temperature from Figure 6 may be used to make this determination, provided that the accuracy of the in-stack temperature sensor is $\pm 1^\circ\text{C}$ (2°F).

10.7 Conversion factors:

From	To	Multiply by
scf	m^3	0.02832
g/ft^3	gr/ft^3	15.43
g/ft^3	lb/ft^3	2.205×10^{-3}
g/ft^3	g/m^3	35.31

10.8 Isokinetic variation:

10.8.1 Calculation from raw data:

$$I = \frac{100 T_s [K_3 F_{lc} + (V_m/T_m) (P_{bar} + \Delta H/13.6)]}{60 B V_s P_s A_n} \quad (4)$$

where:

$K_3 = 0.003454 \text{ mm Hg-m}^3/\text{mL-K}$ for metric units, or
 $K_3 = 0.002669 \text{ in. Hg-ft}^3/\text{mL-}^\circ\text{R}$ for English units.

10.8.2 Calculation for intermediate values:

$$I = \frac{T_s V_m(\text{std}) P_{\text{std}} 100}{T_{\text{std}} V_s B A_n P_s 60 (1 - B_{ws})} \quad (5)$$

$$= K_4 \frac{T_s V_m(\text{std})}{P_s V_s A_n B (1 - B_{ws})}$$

where:

$K_4 = 4.320$ for metric units, or
 $K_4 = 0.09450$ for English units.

10.8.3 Acceptable results: If $90\% \leq I \leq 110\%$, the results are acceptable. If the results are low in comparison with the standard and I is beyond the acceptable range, or if I is less than 90%, the Administrator may opt to accept the results.

10.9 To determine the minimum sample volume that shall be collected, the following sequence of calculations shall be used.

10.9.1 From prior analysis of the waste feed, the concentration of POHCs introduced into the combustion system can be calculated. The degree of destruction and removal efficiency that is required is used to determine the maximum amount of POHC allowed to be present in the effluent. This may be expressed as:

$$\frac{(WF) (POHC_i \text{ conc}) (100 - \%DRE)}{100} = \text{Max POHC}_i \text{ Mass} \quad (6)$$

where:

WF = mass flow rate of waste feed per hr, g/hr (lb/hr).

POHC_i = concentration of Principal Organic Hazardous Compound (wt %) introduced into the combustion process.

DRE = percent Destruction and Removal Efficiency required.

Max POHC = mass flow rate (g/hr [lb/hr]) of POHC emitted from the combustion source.

10.9.2 The average discharge concentration of the POHC in the effluent gas is determined by comparing the Max POHC with the volumetric flow rate being exhausted from the source. Volumetric flow rate data are available as a result of preliminary Method 1-4 determinations:

$$\frac{\text{Max POHC}_i \text{ Mass}}{DV_{\text{eff}}(\text{std})} = \text{Max POHC}_i \text{ conc} \quad (7)$$

where:

$DV_{\text{eff}}(\text{std})$ = volumetric flow rate of exhaust gas, dscm (dscf).

$\text{POHC}_i \text{ conc}$ = anticipated concentration of the POHC in the exhaust gas stream, g/dscm (lb/dscf).

10.9.3 In making this calculation, it is recommended that a safety margin of at least ten be included:

$$\frac{LDL_{\text{POHC}} \times 10}{\text{POHC}_i \text{ conc}} = V_{\text{TBC}} \quad (8)$$

where:

LDL_{POHC} = detectable amount of POHC in entire sampling train.

NOTE: The whole extract from an XAD-2 cartridge is seldom if ever, injected at once. Therefore, if aliquoting factors are involved, the LDL_{POHC} is not the same as the analytical (or column) detection limit.

V_{TBC} = minimum dry standard volume to be collected at dry-gas meter.

10.10 Concentration of any given POHC in the gaseous emissions of a combustion process:

1) Multiply the concentration of the POHC as determined in Method 8270 by the final concentration volume, typically 10 mL.

$$C_{\text{POHC}} (\text{ug/mL}) \times \text{sample volume (mL)} = \text{amount (ug) of POHC in sample} \quad (9)$$

where:

C_{POHC} = concentration of POHC as analyzed by Method 8270.

2) Sum the amount of POHC found in all samples associated with a single train.

$$\text{Total (ug)} = \text{XAD-2 (ug)} + \text{condensate (ug)} + \text{rinses (ug)} + \text{impinger (ug)} \quad (10)$$

3) Divide the total ug found by the volume of stack gas sampled (m³).

$$(\text{Total ug})/(\text{train sample volume}) = \text{concentration of POHC (ug/m}^3\text{)} \quad (11)$$

11.0 QUALITY CONTROL

11.1 Sampling: See EPA Manual 600/4-77-027b for Method 5 quality control.

11.2 Analysis: The quality assurance program required for this study includes the analysis of field and method blanks, procedure validations, incorporation of stable labeled surrogate compounds, quantitation versus stable labeled internal standards, capillary column performance checks, and external performance tests. The surrogate spiking compounds selected for a particular analysis are used as primary indicators of the quality of the analytical data for a wide range of compounds and a variety of sample matrices. The assessment of combustion data, positive identification, and quantitation of the selected compounds are dependent on the integrity of the samples received and the precision and accuracy of the analytical methods employed. The quality assurance procedures for this method are designed to monitor the performance of the analytical method and to provide the required information to take corrective action if problems are observed in laboratory operations or in field sampling activities.

11.2.1 Field Blanks: Field blanks must be submitted with the samples collected at each sampling site. The field blanks include the sample bottles containing aliquots of sample recovery solvents, unused filters, and resin cartridges. At a minimum, one complete sampling train will be assembled in the field staging area, taken to the sampling area, and leak-checked at the beginning and end of the testing (or for the same total number of times as the actual test train). The filter housing and probe of the blank train will be heated during the sample test. The train will be recovered as if it were an actual test sample. No gaseous sample will be passed through the sampling train.

11.2.2 Method blanks: A method blank must be prepared for each set of analytical operations, to evaluate contamination and artifacts that can be derived from glassware, reagents, and sample handling in the laboratory.

11.2.3 Refer to Method 8270 for additional quality control considerations.

12.0 METHOD PERFORMANCE

12.1 Method performance evaluation: Evaluation of analytical procedures for a selected series of compounds must include the sample-preparation procedures and each associated analytical determination. The analytical procedures should be challenged by the test compounds spiked at appropriate levels and carried through the procedures.

12.2 Method detection limit: The overall method detection limits (lower and upper) must be determined on a compound-by-compound basis because different compounds may exhibit different collection, retention, and extraction efficiencies as well as instrumental minimum detection limit (MDL). The method detection limit must be quoted relative to a given sample volume. The upper limits for the method must be determined relative to compound retention volumes (breakthrough).

12.3 Method precision and bias: The overall method precision and bias must be determined on a compound-by-compound basis at a given concentration level. The method precision value would include a combined variability due to sampling, sample preparation, and instrumental analysis. The method bias would be dependent upon the collection, retention, and extraction efficiency of the train components. From evaluation studies to date using a dynamic spiking system, method biases of -13% and -16% have been determined for toluene and 1,1,2,2-tetrachloroethane, respectively. A precision of 19.9% was calculated from a field test data set representing seven degrees of freedom which resulted from a series of paired, unspiked Semivolatile Organic Sampling trains (Semi-VOST) sampling emissions from a hazardous waste incinerator.

13.0 REFERENCES

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Revision 0
Date September 1986

MULTI-METALS

Section 3.0
SAMPLING AND ANALYTICAL METHODS

3.1 Methodology for the Determination of Metals Emissions in Exhaust Gases from Hazardous Waste Incineration and Similar Combustion Processes

3.1.1 Applicability and Principle

3.1.1.1. Applicability. This method is being developed for the determination of total chromium (Cr), cadmium (Cd), arsenic (As), nickel (Ni), manganese (Mn), beryllium (Be), copper (Cu), zinc (Zn), lead (Pb), selenium (Se), phosphorus (P), thallium (Tl), silver (Ag), antimony (Sb), barium (Ba), and mercury (Hg) stack emissions from hazardous waste incinerators and similar combustion processes. This method may also be used for the determination of particulate emissions following the procedures and precautions described. Modifications to the sample recovery and analysis procedures described in this protocol for the purpose of determining particulate emissions may potentially impact the front-half mercury determination. Mercury emissions should be determined using EPA Method 101A given in 40 CFR Part 61.

3.1.1.2 Principle. The stack sample is withdrawn isokinetically from the source, with particulate emissions collected in the probe and on a heated filter and gaseous emissions collected in a series of chilled impingers containing an aqueous solution of dilute nitric acid combined with dilute hydrogen peroxide in each of two impingers, and acidic potassium permanganate solution in each of two impingers. Sampling train components are recovered and digested in separate front- and back-half fractions. Materials collected in the sampling train are digested with acid solutions to dissolve organics and to remove organic constituents that may create analytical interferences. Acid digestion is performed using conventional Parr[®] Bomb or microwave digestion techniques. The nitric acid and hydrogen peroxide impinger solution, the acidic potassium permanganate impinger solution, the HCl rinse solution, and the probe rinse and digested filter solutions are analyzed for mercury by cold vapor atomic absorption spectroscopy (CVAAS). The nitric acid

and hydrogen peroxide solution and the probe rinse and digested filter solutions of the train catches are analyzed for Cr, Cd, Ni, Mn, Be, Cu, Zn, Pb, Se, P, Tl, Ag, Sb, Ba, and As by inductively coupled argon plasma emission spectroscopy (ICAP) or atomic absorption spectroscopy (AAS). Graphite furnace atomic absorption spectroscopy (GFAAS) is used for analysis of antimony, arsenic, cadmium, lead, selenium, and thallium, if these elements require greater analytical sensitivity than can be obtained by ICAP. Additionally, if desired, the tester may use AAS for analyses of all metals if the resulting in-stack-method detection limits meet the goal of the testing program. For convenience, aliquots of each digested sample Fraction 1A plus Fraction 2A can be combined proportionally with respect to the original Fraction 1 (normally diluted to 300 ml following digestion and prior to analysis) Section 3.1.5.3.3; and concentrated Fraction 2A (normally diluted to 150 ml following digestion and prior to analysis) Section 3.1.5.3.4.1 or 3.1.5.3.4.2 for a single analytical determination. The efficiency of the analytical procedure is quantified by the analysis of spiked quality control samples containing each of the target metals and/or other quality assurance measures, as necessary, including actual sample matrix effects checks.

3.1.2 Range, Sensitivity, Precision, and Interferences

3.1.2.1 Range. For the analyses described in this methodology and for similar analyses, the ICAP response is linear over several orders of magnitude. Samples containing metal concentrations in the nanograms per milliliter (ng/ml) to micrograms per milliliter ($\mu\text{g/ml}$) range in the analytical finish solution can be analyzed using this technique. Samples containing greater than approximately 50 $\mu\text{g/ml}$ of chromium, lead, or arsenic should be diluted to that level or lower for final analysis. Samples containing greater than approximately 20 $\mu\text{g/ml}$ of cadmium should be diluted to that level before analysis.

3.1.2.2 Analytical Sensitivity. ICAP analytical detection limits for the sample solutions (based on SW-846, Method 6010) are approximately as follows: Sb (32 ng/ml), As (53 ng/ml), Ba (2 ng/ml), Be (0.3 ng/ml), Cd (4 ng/ml), Cr (7 ng/ml), Cu (6 ng/ml), Pb (42 ng/ml), Mn (2 ng/ml), Ni (15

ng/ml), P (75 ng/ml), Se (75 ng/ml), Ag (7 ng/ml), Tl (40 ng/ml), and Zn (2 ng/ml). The actual method detection limits are sample dependent and may vary as the sample matrix may affect the limits. The analytical detection limits for analysis by direct aspiration AAS (based on SW-846, Method 7000 series) are approximately as follows: Sb (200 ng/ml), As (2 ng/ml), Ba (100 ng/ml), Be (5 ng/ml), Cd (5 ng/ml), Cr (50 ng/ml), Cu (20 ng/ml), Pb (100 ng/ml), Mn (10 ng/ml), Ni (40 ng/ml), Se (2 ng/ml), Ag (10 ng/ml), Tl (100 ng/ml), and Zn (5 ng/ml). The detection limit for mercury by CVAAS is approximately 0.2 ng/ml). The use of GFAAS can give added sensitivity compared to the use of direct aspiration AAS for the following metals: Sb (3 ng/ml), As (1 ng/ml), Be (0.2 ng/ml), Cd (0.1 ng/ml), Cr (1 ng/ml), Pb (1 ng/ml), Se (2 ng/ml), and Tl (1 ng/ml).

Using (1) the procedures described in this method, (2) the analytical detection limits described in the previous paragraph, (3) a volume of 300 ml, Fraction 1, for the front half and 150 ml, Fraction 2A, for the back-half samples, and (4) a stack gas sample volume of 1.25 m³, the corresponding in-stack method detection limits are presented in Table A-1 and calculated as shown:

$$\frac{A \times B}{C} = D$$

where: A = analytical detection limit, µg/ml.
 B = volume of sample prior to aliquot for analysis, ml.
 C = stack sample volume, dscm (dsm³).
 D = in-stack detection limit, µg/m³.

Values in Table 3.1-1 are calculated for the front and back half and/or the total train.

To ensure optimum sensitivity in obtaining the measurements, the concentrations of target metals in the solutions are suggested to be at least ten times the analytical detection limits. Under certain conditions, and with greater care in the analytical procedure, this concentration can be as low as approximately three times the analytical detection limit. In all cases, on at

least one sample (run) in the source test and for each metal analyzed, repetitive analyses, method of standard additions (MSA), serial dilution, or matrix spike addition, etc., shall be used to establish the quality of the data.

Actual in-stack method detection limits will be determined based on actual source sampling parameters and analytical results as described above. If required, the method in-stack detection limits can be made more sensitive than those shown in Table A-1 for a specific test by using one or more of the following options:

- A 1-hour sampling run may collect a stack gas sampling volume of about 1.25 m³. If the sampling time is increased and 5 m³ are collected, the in-stack method detection limits would be one fourth of the values shown in Table A-1 (this means that with this change, the method is four times more sensitive than a 1-hour run. Larger sample volumes (longer runs) would make it even more sensitive).
- The in-stack detection limits assume that all of the sample is digested (with exception of the aliquot for mercury) and the final liquid volumes for analysis are 300 ml, Fraction 1 for the front half and 150 ml, Fraction 2A, for the back-half sample. If the front-half volume is reduced from 300 ml to 30 ml, the front-half in-stack detection limits would be one tenth of the values shown above (ten times more sensitive). If the back-half volume is reduced from 150 ml to 25 ml, the in-stack detection limits would be one sixth of the above values. Matrix effects checks are necessary on analyses of samples and typically are of greater significance for samples that have been concentrated to less than the normal original sample volume. Reduction to a volume of less than 25 ml may not allow redissolving of the residue and may increase interference by other compounds.
- When both of the above two improvements are used on one sample at the same time, the resultant improvements are multiplicative. For example, where stack gas volume is increased by a factor of five and the total liquid sample digested volume of both the front and back halves is reduced by a factor of six, the in-stack method detection limit is reduced by a factor of thirty (the method is thirty times more sensitive).

Table 3.1-1

IN-STACK METHOD DETECTION LIMITS ($\mu\text{g}/\text{m}^3$)
FOR TRAIN FRACTIONS USING ICAP AND AAS

Metal	Front-half Fraction 1 Probe and Filter	Back-half Fraction 2 Impingers 1-3	Back-half Fractions "Hg, only" Impingers 4-6	Total Train
Antimony	7.7 (0.7)*	3.8 (0.4)*		11.5 (1.1)*
Arsenic	12.7 (0.3)*	6.4 (0.1)*		19.1 (0.4)*
Barium	0.5	0.3		0.8
Beryllium	0.07 (0.05)*	0.04 (0.03)*		0.11 (0.08)*
Cadmium	1.0 (0.02)*	0.5 (0.01)*		1.5 (0.03)*
Chromium	1.7 (0.2)*	0.8 (0.1)*		2.5 (0.3)*
Copper	1.4	0.7		2.1
Lead	10.1 (0.2)*	5.0 (0.1)*		15.1 (0.3)*
Manganese	0.5 (0.2)*	0.2 (0.1)*		0.7 (0.3*)
Mercury	0.6**	3.0**	2.0**	5.6**
Nickel	3.6	1.8		5.4
Phosphorus	18	9		27
Selenium	18 (0.5)*	9 (0.3)*		27 (0.8)*
Silver	1.7	0.9		2.6
Thallium	9.6 (0.2)*	4.8 (0.1)*		14.4 (0.3)*
Zinc	0.5	0.3		0.8

(*)* Detection limit when analyzed by GFAAS.

** Detection limit when analyzed by CVAAS, estimated for Back Half and Total Train.

Note: Actual method in-stack detection limits will be determined based on actual source sampling parameters and analytical results as described earlier in this section.

- Conversely, reducing stack gas sample volume and increasing sample liquid volume will increase in-stack detection limits (the method would then be less sensitive). The front-half and back-half samples (Fractions 1A plus and 2A) can be combined proportionally (see Section 3.1.1.2 of this methodology) prior to analysis. The resultant liquid volume (excluding the mercury fractions, which must be analyzed separately) is recorded. Combining the sample as described does not allow determination (whether front or back half) of where in the train the sample was captured. The in-stack method detection limit then becomes a single value for all metals except mercury, for which the contribution of the mercury fractions must be considered.
- The above discussion assumes no blank correction. Blank corrections are discussed later in this method.

3.1.2.3 Precision. The precisions (relative standard deviation) for each metal detected in a method development test at a sewage sludge incinerator, are as follows: Sb (12.7%), As (13.5%), Ba (20.6%), Cd (11.5%), Cr (11.2%), Cu (11.5%), Pb (11.6%), P (14.6%), Se (15.3%), Tl (12.3%), and Zn (11.8%). The precision for nickel was 7.7% for another test conducted at a source simulator. Beryllium, manganese, and silver were not detected in the tests; however, based on the analytical sensitivity of the ICAP for these metals, it is assumed that their precisions should be similar to those for the other metals, when detected at similar levels.

3.1.2.4 Interferences. Iron can be a spectral interference during the analysis of arsenic, chromium, and cadmium by ICAP. Aluminum can be a spectral interference during the analysis of arsenic and lead by ICAP. Generally, these interferences can be reduced by diluting the sample, but this increases the method detection limit (in-stack detection limit). Refer to EPA Method 6010 (SW-846) or the other analytical methods used for details on potential interferences for this method. The analyst must eliminate or reduce interferences to acceptable levels. For all GFAAS analyses, matrix modifiers should be used to limit interferences, and standards should be matrix matched.

3.1.3 Apparatus

3.1.3.1 Sampling Train. A schematic of the sampling train is shown in Figure 3.1-1. It is similar to the 40 CFR Part 60, Appendix A Method 5 train. The sampling train consists of the following components:

3.1.3.1.1 Probe Nozzle (Probe Tip) and Borosilicate or Quartz Glass Probe Liner. Same as Method 5, Sections 2.1.1 and 2.1.2, except that glass nozzles are required unless an alternate probe tip prevents the possibility of contamination or interference of the sample with its materials of construction. If a probe tip other than glass is used, no correction (because of any effect on the sample by the probe tip) of the stack-sample test results can be made.

3.1.3.1.2 Pitot Tube and Differential Pressure Gauge. Same as Method 2, Sections 2.1 and 2.2, respectively.

3.1.3.1.3 Filter Holder. Glass, same as Method 5, Section 2.1.5, except that a Teflon filter support or other non-metallic, non-contaminating support must be used to replace the glass frit.

3.1.3.1.4 Filter Heating System. Same as Method 5, Section 2.1.6.

3.1.3.1.5 Condenser. The following system shall be used for the condensation and collection of gaseous metals and for determining the moisture content of the stack gas. The condensing system should consist of four to seven impingers connected in series with leak-free ground glass fittings or other leak-free, non-contaminating fittings. The first impinger is optional and is recommended as a moisture knockout trap for use during test conditions which require such a trap. The first impinger shall be appropriately-sized, if necessary, for an expected large moisture catch and generally constructed as described for the first impinger in Method 5, Paragraph 2.1.7. The second impinger (or the first $\text{HNO}_3/\text{H}_2\text{O}_2$ impinger) shall also be constructed as described for the first impinger in Method 5. The third impinger (or the second $\text{HNO}_3/\text{H}_2\text{O}_2$ impinger) shall be the same as the Greenburg Smith impinger

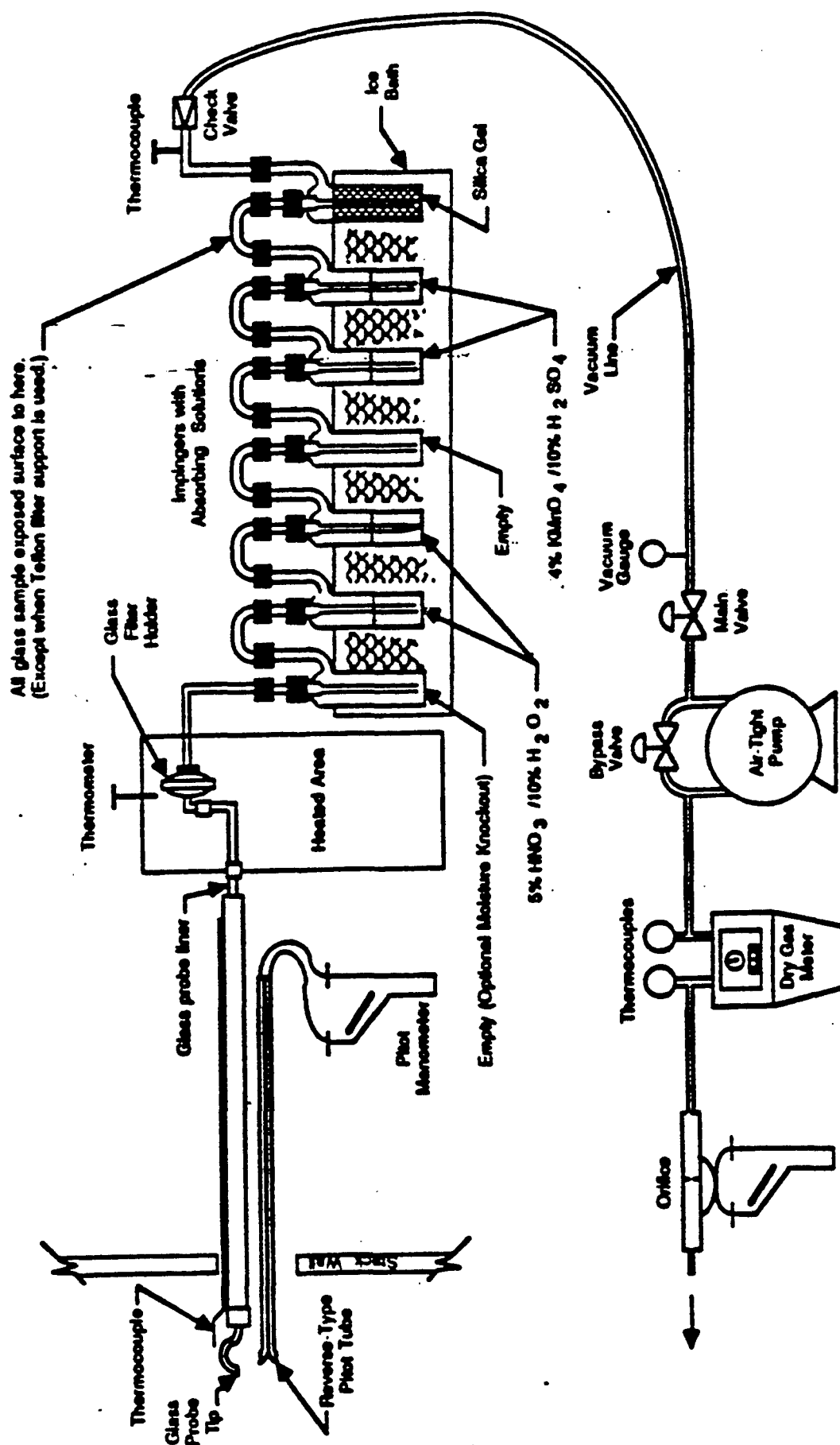


Figure 3.1-1 Schematic of multiple metals sampling train configuration.

with the standard tip described as the second impinger in Method 5, Paragraph 2.1.7. All other impingers used in the methods train are the same as the first $\text{HNO}_3/\text{H}_2\text{O}_2$ impinger described in this paragraph. In summary, the first impinger which may be optional as described in this methodology shall be empty, the second and third shall contain known quantities of a nitric acid/hydrogen peroxide solution (Section 3.1.4.2.1), the fourth shall be empty, the fifth and sixth shall contain a known quantity of acidic potassium permanganate solution (Section 3.1.4.2.2), and the last impinger shall contain a known quantity of silica gel. A thermometer capable of measuring to within 1°C (2°F) shall be placed at the outlet of the last impinger. When the moisture knockout impinger is not needed, it is removed from the train and the other impingers remain the same. If mercury analysis is not to be performed, the potassium permanganate impingers and the empty impinger preceding them are removed.

3.1.3.1.6 Metering System, Barometer, and Gas Density Determination Equipment. Same as Method 5, Sections 2.1.8 through 2.1.10, respectively.

3.1.3.1.7 Teflon Tape. For capping openings and sealing connections, if necessary, on the sampling train.

3.1.3.2 Sample Recovery. Same as Method 5, Sections 2.2.1 through 2.2.8 (Nonmetallic Probe-Liner and Probe-Nozzle Brushes or Swabs, Wash Bottles, Sample Storage Containers, Petri Dishes, Glass Graduated Cylinder, Plastic Storage Containers, Funnel and Rubber Policeman, and Glass Funnel), respectively, with the following exceptions and additions:

3.1.3.2.1 Nonmetallic Probe-Liner and Probe-Nozzle Brushes or Swabs. For quantitative recovery of materials collected in the front half of the sampling train. Description of acceptable all-Teflon component brushes or swabs is to be included in EPA's Emission Measurement Technical Information Center (EMTIC) files.

3.1.3.2.2 Sample Storage Containers. Glass bottles with Teflon-lined caps which are non-reactive to the oxidizing solutions, with a capacity

of 1000- and 500-ml, shall be used for KMnO_4 -containing samples and blanks. Polyethylene bottles may be used for other sample types.

3.1.3.2.3 Graduated Cylinder. Glass or equivalent.

3.1.3.2.4 Funnel. Glass or equivalent.

3.1.3.2.5 Labels. For identification of samples.

3.1.3.2.6 Polypropylene Tweezers and/or Plastic Gloves. For recovery of the filter from the sampling train filter holder.

3.1.3.3 Sample Preparation and Analysis. For the analysis, the following equipment is needed:

3.1.3.3.1 Volumetric Flasks, 100-ml, 250-ml, and 1000-ml. For preparation of standards and sample dilution.

3.1.3.3.2 Graduated Cylinders. For preparation of reagents.

3.1.3.3.3 Parr² Bombs or Microwave Pressure Relief Vessels with Capping Station (CEM Corporation model or equivalent).

3.1.3.3.4 Beakers and Watchglasses. 250-ml beakers for sample digestion with watchglasses to cover the tops.

3.1.3.3.5 Ring Stands and Clamps. For securing equipment such as filtration apparatus.

3.1.3.3.6 Filter Funnels. For holding filter paper.

3.1.3.3.7 Whatman 541 Filter Paper (or equivalent). For filtration of digested samples.

3.1.3.3.8 Disposable Pasteur Pipets and Bulbs.

3.1.3.3.9 Volumetric Pipets.

3.1.3.3.10 Analytical Balance. Accurate to within 0.1 mg.

3.1.3.3.11 Microwave or Conventional Oven. For heating samples at fixed power levels or temperatures.

3.1.3.3.12 Hot Plates.

3.1.3.3.13 Atomic Absorption Spectrometer (AAS). Equipped with a background corrector.

3.1.3.3.13.1 Graphite Furnace Attachment. With antimony, arsenic, cadmium, lead, selenium, thallium hollow cathode lamps (HCLs) or electrodeless discharge lamps (EDLs). [Same as EPA SW-846 Methods 7041 (antimony), 7060 (arsenic), 7131 (cadmium), 7421 (lead), 7740 (selenium), and 7841 (thallium).]

3.1.3.3.13.2 Cold Vapor Mercury Attachment. With a mercury HCL or EDL. The equipment needed for the cold vapor mercury attachment includes an air recirculation pump, a quartz cell, an aerator apparatus, and a heat lamp or desiccator tube. The heat lamp should be capable of raising the ambient temperature at the quartz cell by 10°C such that no condensation forms on the wall of the quartz cell. (Same as EPA Method 7470.)

3.1.3.3.14 Inductively Coupled Argon Plasma Spectrometer. With either a direct or sequential reader and an alumina torch. (Same as EPA Method 6010.)

3.1.4 Reagents

The complexity of this methodology is such that to obtain reliable results, the testers (including analysts) should be experienced and knowledgeable in source sampling, in handling and preparing (including mixing) reagents as described, and using adequate safety procedures and protective equipment in performing this method, including sampling, mixing reagents, digestions, and

analyses. Unless otherwise indicated, it is intended that all reagents conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available; otherwise, use the best available grade.

3.1.4.1 Sampling. The reagents used in sampling are as follows:

3.1.4.1.1 Filters. The filters shall contain less than $1.3 \mu\text{g}/\text{in}^2$ of each of the metals to be measured. Analytical results provided by filter manufacturers are acceptable. However, if no such results are available, filter blanks must be analyzed for each target metal prior to emission testing. Quartz fiber or glass fiber (which meet the requirement of containing less than $1.3 \mu\text{g}/\text{in}^2$ of each metal) filters without organic binders shall be used. The filters should exhibit at least 99.95 percent efficiency (<0.05 percent penetration) on 0.3 micron dioctyl phthalate smoke particles. The filter efficiency test shall be conducted in accordance with ASTM Standard Method D2986-71 (incorporated by reference). For particulate determination in sources containing SO_2 or SO_3 , the filter material must be of a type that is unreactive to SO_2 or SO_3 , as described in EPA Method 5. Quartz fiber filters meeting these requirements are recommended for use in this method.

3.1.4.1.2 Water. To conform to ASTM Specification D1193.77, Type II (incorporated by reference). If necessary, analyze the water for all target metals prior to field use. All target metal concentrations should be less than 1 ng/ml.

3.1.4.1.3 Nitric Acid. Concentrated. Baker Instra-analyzed or equivalent.

3.1.4.1.4 Hydrochloric Acid. Concentrated. Baker Instra-analyzed or equivalent.

3.1.4.1.5 Hydrogen Peroxide, 30 Percent (V/V).

3.1.4.1.6 Potassium Permanganate.

3.1.4.1.7 Sulfuric Acid. Concentrated.

3.1.4.1.8 Silica Gel and Crushed Ice. Same as Method 5, Sections 3.1.2 and 3.1.4, respectively.

3.1.4.2 Pretest Preparation for Sampling Reagents.

3.1.4.2.1 Nitric Acid (HNO_3)/Hydrogen Peroxide (H_2O_2) Absorbing Solution, 5 Percent HNO_3 /10 Percent H_2O_2 . Carefully with stirring, add 50 ml of concentrated HNO_3 to a 1000-ml volumetric flask containing approximately 500 ml of water, and then, carefully with stirring, add 333 ml of 30 percent H_2O_2 . Dilute to volume (1000 ml) with water. Mix well. The reagent shall contain less than 2 ng/ml of each target metal.

3.1.4.2.2 Acidic Potassium Permanganate (KMnO_4) Absorbing Solution, 4 Percent KMnO_4 (W/V), 10 Percent H_2SO_4 (V/V). Prepare fresh daily. Mix carefully, with stirring, 100 ml of concentrated H_2SO_4 into 800 ml of water, and add water with stirring to make a volume of 1 L: this solution is 10 percent H_2SO_4 (V/V). Dissolve, with stirring, 40 g of KMnO_4 into 10 percent H_2SO_4 (V/V) and add 10 percent H_2SO_4 (V/V) with stirring to make a volume of 1 L: this is the acidic potassium permanganate absorbing solution. Prepare and store in glass bottles to prevent degradation. The reagent shall contain less than 2 ng/ml of Hg.

Precaution: To prevent autocatalytic decomposition of the permanganate solution, filter the solution through Whatman 541 filter paper. Also, due to the potential reaction of the potassium permanganate with the acid, there may be pressure buildup in the sample storage bottle; these bottles shall not be fully filled and shall be vented both to relieve potential excess pressure and prevent explosion due to pressure buildup. Venting is required, but should not allow contamination of the sample; a No. 70-72 hole drilled in the container cap and Teflon liner has been used.

3.1.4.2.3 Nitric Acid, 0.1 N. With stirring, add 6.3 ml of concentrated HNO_3 (70 percent) to a flask containing approximately 900 ml of water. Dilute to 1000 ml with water. Mix well. The reagent shall contain less than 2 ng/ml of each target metal.

3.1.4.2.4 Hydrochloric Acid (HCl), 8 N. Make the desired volume of 8 N HCl in the following proportions. Carefully with stirring, add 690 ml of concentrated HCl to a flask containing 250 ml of water. Dilute to 1000 ml with water. Mix well. The reagent shall contain less than 2 ng/ml of Hg.

3.1.4.3 Glassware Cleaning Reagents.

3.1.4.3.1 Nitric Acid, Concentrated. Fisher ACS grade or equivalent.

3.1.4.3.2 Water. To conform to ASTM Specifications D1193-77, Type II.

3.1.4.3.3 Nitric Acid, 10 Percent (V/V). With stirring, add 500 ml of concentrated HNO_3 to a flask containing approximately 4000 ml of water. Dilute to 5000 ml with water. Mix well. Reagent shall contain less than 2 ng/ml of each target metal.

3.1.4.4 Sample Digestion and Analysis Reagents.

3.1.4.4.1 Hydrochloric Acid, Concentrated.

3.1.4.4.2 Hydrofluoric Acid, Concentrated.

3.1.4.4.3 Nitric Acid, Concentrated. Baker Instra-analyzed or equivalent.

3.1.4.4.4 Nitric Acid, 50 Percent (V/V). With stirring, add 125 ml of concentrated HNO_3 to 100 ml of water. Dilute to 250 ml with water. Mix well. Reagent shall contain less than 2 ng/ml of each target metal.

3.1.4.4.5 Nitric Acid, 5 Percent (V/V). With stirring, add 50 ml of concentrated HNO_3 to 800 ml of water. Dilute to 1000 ml with water. Mix well. Reagent shall contain less than 2 ng/ml of each target metal.

3.1.4.4.6 Water. To conform to ASTM Specifications D1193-77, Type II.

3.1.4.4.7 Hydroxylamine Hydrochloride and Sodium Chloride Solution. See EPA Method 7470 for preparation.

3.1.4.4.8 Stannous Chloride. See Method 7470.

3.1.4.4.9 Potassium Permanganate, 5 Percent (W/V). See Method 7470.

3.1.4.4.10 Sulfuric Acid, Concentrated.

3.1.4.4.11 Nitric Acid, 50 Percent (V/V).

3.1.4.4.12 Potassium Persulfate, 5 Percent (W/V). See Method 7470.

3.1.4.4.13 Nickel Nitrate, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$.

3.1.4.4.14 Lanthanum, Oxide, La_2O_3 .

3.1.4.4.15 AAS Grade Hg Standard, 1000 $\mu\text{g}/\text{ml}$.

3.1.4.4.16 AAS Grade Pb Standard, 1000 $\mu\text{g}/\text{ml}$.

3.1.4.4.17 AAS Grade As Standard, 1000 $\mu\text{g}/\text{ml}$.

3.1.4.4.18 AAS Grade Cd Standard, 1000 $\mu\text{g}/\text{ml}$.

3.1.4.4.19 AAS Grade Cr Standard, 1000 $\mu\text{g}/\text{ml}$.

3.1.4.4.20 AAS Grade Sb Standard, 1000 $\mu\text{g/ml}$.

3.1.4.4.21 AAS Grade Ba Standard, 1000 $\mu\text{g/ml}$.

3.1.4.4.22 AAS Grade Be Standard, 1000 $\mu\text{g/ml}$.

3.1.4.4.23 AAS Grade $\text{C}\mu$ Standard, 1000 $\mu\text{g/ml}$.

3.1.4.4.24 AAS Grade Mn Standard, 1000 $\mu\text{g/ml}$.

3.1.4.4.25 AAS Grade Ni Standard, 1000 $\mu\text{g/ml}$.

3.1.4.4.26 AAS Grade P Standard, 1000 $\mu\text{g/ml}$.

3.1.4.4.27 AAS Grade Se Standard, 1000 $\mu\text{g/ml}$.

3.1.4.4.28 AAS Grade Ag Standard, 1000 $\mu\text{g/ml}$.

3.1.4.4.29 AAS Grade Tl Standard, 1000 $\mu\text{g/ml}$.

3.1.4.4.30 AAS Grade Zn Standard, 1000 $\mu\text{g/ml}$.

3.1.4.4.31 AAS Grade Al Standard, 1000 $\mu\text{g/ml}$.

3.1.4.4.32 AAS Grade Fe Standard, 1000 $\mu\text{g/ml}$.

3.1.4.4.33 The metals standards may also be made from solid chemicals as described in EPA Method 200.7. EPA SW-846 Method 7470 or Standard Methods for the Analysis of Water and Wastewater, 15th Edition, Method 303F should be referred to for additional information on mercury standards.

3.1.4.4.34 Mercury Standards and Quality Control Samples. Prepare fresh weekly a 10 $\mu\text{g/ml}$ intermediate mercury standard by adding 5 ml of 1000 $\mu\text{g/ml}$ mercury stock solution to a 500-ml volumetric flask; dilute with

stirring to 500 ml by first carefully adding 20 ml of 15 percent HNO_3 and then adding water to the 500-ml volume. Mix well. Prepare a 200 ng/ml working mercury standard solution fresh daily: add 5 ml of the 10 $\mu\text{g/ml}$ intermediate standard to a 250-ml volumetric flask and dilute to 250 ml with 5 ml of 4 percent KMnO_4 , 5 ml of 15 percent HNO_3 , and then water. Mix well. At least six separate aliquots of the working mercury standard solution should be used to prepare the standard curve. These aliquots should contain 0.0, 1.0, 2.0, 3.0, 4.0, and 5.0 ml of the working standard solution containing 0, 200, 400, 600, 800, and 1000 ng mercury, respectively. Quality control samples should be prepared by making a separate 10 $\mu\text{g/ml}$ standard and diluting until in the range of the calibration.

3.1.4.4.35 ICAP Standards and Quality Control Samples. Calibration standards for ICAP analysis can be combined into four different mixed standard solutions as shown below.

MIXED STANDARD SOLUTIONS FOR ICAP ANALYSIS

Solution	Elements
I	As, Be, Cd, Mn, Pb, Se, Zn
II	Ba, Cu, Fe
III	Al, Cr, Ni
IV	Ag, P, Sb, Tl

Prepare these standards by combining and diluting the appropriate volumes of the 1000 $\mu\text{g/ml}$ solutions with 5 percent nitric acid. A minimum of one standard and a blank can be used to form each calibration curve. However, a separate quality control sample spiked with known amounts of the target metals in quantities in the midrange of the calibration curve should be prepared. Suggested standard levels are 25 $\mu\text{g/ml}$ for Al, Cr, and Pb, 15 $\mu\text{g/ml}$ for Fe, and 10 $\mu\text{g/ml}$ for the remaining elements. Standards containing less than 1 $\mu\text{g/ml}$ of metal should be prepared daily. Standards containing greater than 1 $\mu\text{g/ml}$ of metal should be stable for a minimum of 1 to 2 weeks.

3.1.4.4.36 Graphite Furnace AAS Standards. Antimony, arsenic, cadmium, lead, selenium, and thallium. Prepare a 10 $\mu\text{g/ml}$ standard by adding 1 ml of 1000 $\mu\text{g/ml}$ standard to a 100-ml volumetric flask. Dilute with stirring to 100 ml with 10 percent nitric acid. For graphite furnace AAS, the

standards must be matrix matched. Prepare a 100 ng/ml standard by adding 1 ml of the 10 µg/ml standard to a 100-ml volumetric flask and dilute to 100 ml with the appropriate matrix solution. Other standards should be prepared by dilution of the 100 ng/ml standards. At least five standards should be used to make up the standard curve. Suggested levels are 0, 10, 50, 75, and 100 ng/ml. Quality control samples should be prepared by making a separate 10 µg/ml standard and diluting until it is in the range of the samples. Standards containing less than 1 µg/ml of metal should be prepared daily. Standards containing greater than 1 µg/ml of metal should be stable for a minimum of 1 to 2 weeks.

3.1.4.4.37 Matrix Modifiers.

3.1.4.4.37.1 Nickel Nitrate, 1 Percent (V/V). Dissolve 4.956 g of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in approximately 50 ml of water in a 100-ml volumetric flask. Dilute to 100 ml with water.

3.1.4.4.37.2 Nickel Nitrate, 0.1 Percent (V/V). Dilute 10 ml of the 1 percent nickel nitrate solution from Section 4.4.37.1 above to 100 ml with water. Inject an equal amount of sample and this modifier into the graphite furnace during AAS analysis for As.

3.1.4.4.37.3 Lanthanum. Carefully dissolve 0.5864 g of La_2O_3 in 10 ml of concentrated HNO_3 and dilute the solution by adding it with stirring to approximately 50 ml of water, and then dilute to 100 ml with water. Mix well. Inject an equal amount of sample and this modifier into the graphite furnace during AAS analysis for Pb.

3.1.5 Procedure

3.1.5.1 Sampling. The complexity of this method is such that, to obtain reliable results, testers and analysts should be trained and experienced with the test procedures, including source sampling, reagent preparation and handling, sample handling, analytical calculations, reporting, and

descriptions specifically at the beginning of and throughout Section 3.1.4 and all other sections of this methodology.

3.1.5.1.1 Pretest Preparation. Follow the same general procedure given in Method 5, Section 4.1.1, except that, unless particulate emissions are to be determined, the filter need not be desiccated or weighed. All sampling train glassware should first be rinsed with hot tap water and then washed in hot soapy water. Next, glassware should be rinsed three times with tap water, followed by three additional rinses with water. All glassware should then be soaked in a 10 percent (V/V) nitric acid solution for a minimum of 4 hours, rinsed three times with water, rinsed a final time with acetone, and allowed to air dry. All glassware openings where contamination can occur should be covered until the sampling train is assembled for sampling.

3.1.5.1.2 Preliminary Determinations. Same as Method 5, Section 4.1.2.

3.1.5.1.3 Preparation of Sampling Train. Follow the same general procedures given in Method 5, Section 4.1.3, except place 100 ml of the nitric acid/hydrogen peroxide solution (Section 3.1.4.2.1) in each of the two $\text{HNO}_3/\text{H}_2\text{O}_2$ impingers as shown in Figure 3.1-1 (normally the second and third impingers), place 100 ml of the acidic potassium permanganate absorbing solution (Section 3.1.4.2.2) in each of the two permanganate impingers as shown in Figure A-1, and transfer approximately 200 to 300 g of preweighed silica gel from its container to the last impinger. Alternatively, the silica gel may be weighed directly in the impinger just prior to train assembly.

Several options are available to the tester based on the sampling requirements and conditions. The use of an empty first impinger can be eliminated if the moisture to be collected in the impingers will be less than approximately 100 ml. If necessary, use as applicable to this methodology the procedure described in Section 7.1.1 of EPA Method 101A, 40 CFR Part 61, Appendix B, to maintain the desired color in the last permanganate impinger.

Retain for reagent blanks volumes of the nitric acid/hydrogen peroxide solution per Section 3.1.5.2.9 of this method and of the acidic potassium permanganate solution per Section 3.1.5.2.10. These reagent blanks should be labeled and analyzed as described in Section 3.1.7. Set up the sampling train as shown in Figure 3.1-1, or if mercury analysis is not to be performed in the train, then it should be modified by removing the two permanganate impingers and the impinger preceding the permanganate impingers. If necessary to ensure leak-free sampling train connections and prevent contamination Teflon tape or other non-contaminating material should be used instead of silicone grease.....

Precaution: Extreme care should be taken to prevent contamination within the train. Prevent the mercury collection reagent (acidic potassium permanganate) from contacting any glassware of the train which is washed and analyzed for Mn. Prevent hydrogen peroxide from mixing with the acidic potassium permanganate.

Mercury emissions can be measured, alternatively, in a separate train which measures only mercury emissions by using EPA Method 101A with the modifications described below (and with the further modification that the permanganate containers shall be processed as described in the Precaution in Section 3.1.4.2.2 and the Note in Section 3.1.5.2.5 of this methodology). This alternative method is applicable for measurement of mercury emissions, and it may be of special interest to sources which must measure both mercury and manganese emissions.

[Section 7.2.1 of Method 101A shall be modified as follows after the 250 to 400-ml KMnO_4 rinse:

To remove any precipitated material and any residual brown deposits on the glassware following the permanganate rinse, rinse with approximately 100 ml of deionized distilled water, and add this water rinse carefully assuring transfer

of all loose precipitated materials from the three permanganate impingers into the permanganate Container No. 1. If no visible deposits remain after this water rinse, do not rinse with 8 N HCl. However, if deposits do remain on the glassware after this water rinse, wash the impinger surfaces with 25 ml of 8 N HCl, and place the wash in a separate sample container labeled Container No. 1.A. containing 200 ml of water as follows. Place 200 ml of water in a sample container labeled Container No. 1.A. Wash the impinger walls and stem with the HCl by turning the impinger on its side and rotating it so that the HCl contacts all inside surfaces. Use a total of only 25 ml of 8 N HCl for rinsing all permanganate impingers combined. Rinse the first impinger, then pour the actual rinse used for the first impinger into the second impinger for its rinse, etc. Finally, pour the 25 ml of 8 N HCl rinse carefully with stirring into Container No. 1.A. Analyze the HCl rinse separately by carefully diluting with stirring the contents of Container No. 1.A. to 500 ml with deionized distilled water. Filter (if necessary) through Whatman 40 filter paper, and then analyze for mercury according to Section 7.4, except limit the aliquot size to a maximum of 10 ml. Prepare and analyze a water diluted blank 8 N HCl sample by using the same procedure as that used by Container No. 1.A., except add 5 ml of 8 N HCl with stirring to 40 ml of water, and then dilute to 100 ml with water. Then analyze as instructed for the sample from Container No. 1.A. Because the previous separate permanganate solution rinse (Section 7.2.1) and

water rinse (as modified in these guidelines) have the capability to recover a very high percentage of the mercury from the permanganate impingers, the amount of mercury in the HCl rinse in Container No. 1.A. may be very small, possibly even insignificantly small. However, add the total of any mercury analyzed and calculated for the HCl rinse sample Container No. 1.A. to that calculated from the mercury sample from Section 7.3.2 which contains the separate permanganate rinse (and water rinse as modified herein) for calculation of the total sample mercury concentration.

3.1.5.1.4 Leak-Check Procedures. Follow the leak-check procedures given in Method 5, Section 4.1.4.1 (Pretest Leak-Check), Section 4.1.4.2 (Leak-Checks During the Sample Run), and Section 4.1.4.3 (Post-Test Leak-Checks).

3.1.5.1.5 Sampling Train Operation. Follow the procedures given in Method 5, Section 4.1.5. For each run, record the data required on a data sheet such as the one shown in Figure 5-2 of Method 5.

3.1.5.1.6 Calculation of Percent Isokinetic. Same as Method 5, Section 4.1.6.

3.1.5.2 Sample Recovery. Begin cleanup procedures as soon as the probe is removed from the stack at the end of a sampling period.

The probe should be allowed to cool prior to sample recovery. When it can be safely handled, wipe off all external particulate matter near the tip of the probe nozzle and place a rinsed, non-contaminating cap over the probe nozzle to prevent losing or gaining particulate matter. Do not cap the probe tip tightly while the sampling train is cooling. This normally causes a

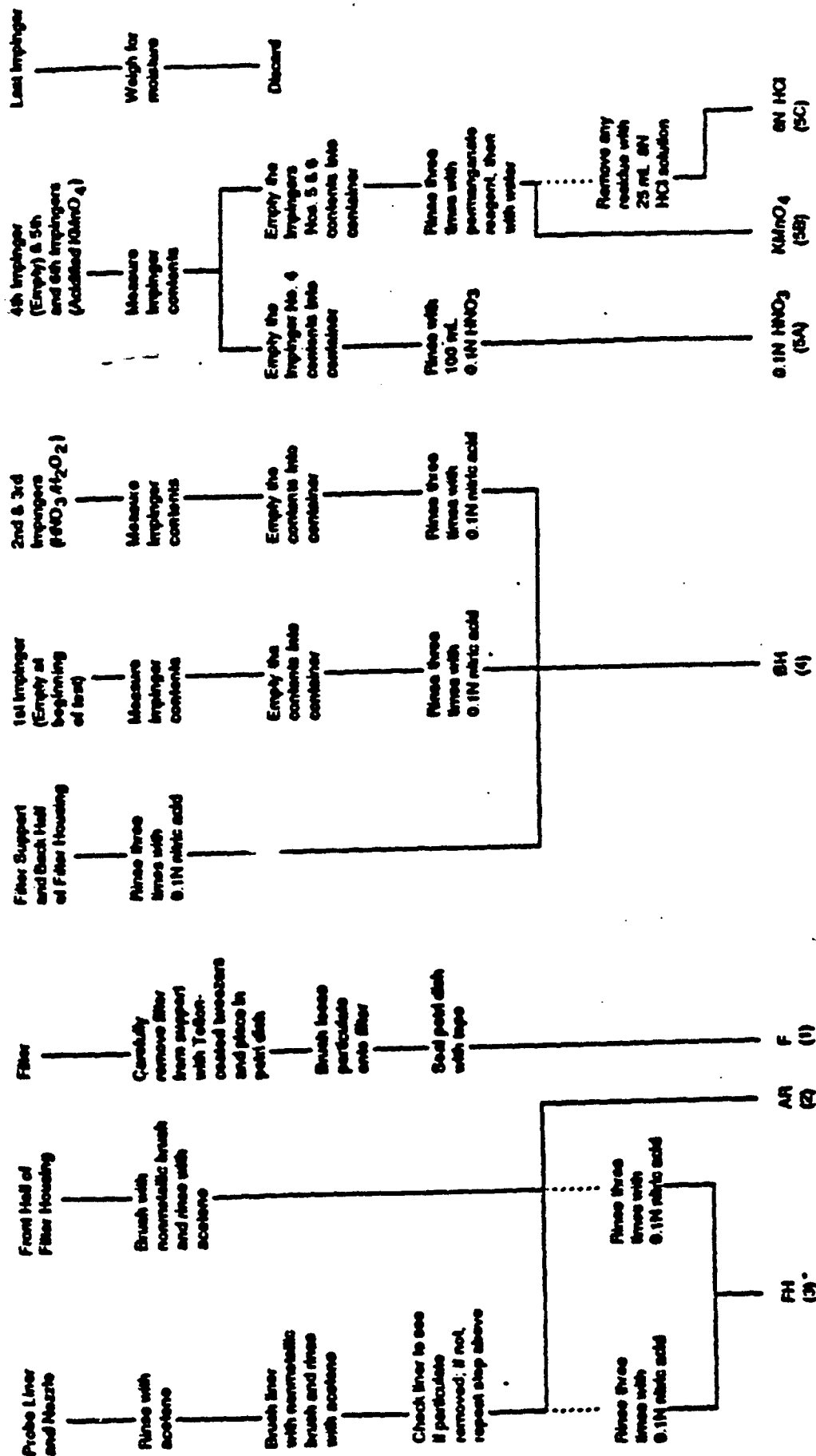
vacuum to form in the filter holder, thus causing the undesired result of drawing liquid from the impingers into the filter.

Before moving the sampling train to the cleanup site, remove the probe from the sampling train and cap the open outlet. Be careful not to lose any condensate that might be present. Cap the filter inlet where the probe was fastened. Remove the umbilical cord from the last impinger and cap the impinger. Cap off the filter holder outlet and impinger inlet. Use non-contaminating caps, whether ground-glass stoppers, plastic caps, serum caps, or Teflon tape to close these openings.

Alternatively, the train can be disassembled before the probe and filter holder/oven are completely cooled, if this procedure is followed: Initially disconnect the filter holder outlet/impinger inlet and loosely cap the open ends. Then disconnect the probe from the filter holder or cyclone inlet and loosely cap the open ends. Cap the probe tip and remove the umbilical cord as previously described.

Transfer the probe and filter-impinger assembly to a cleanup area that is clean and protected from the wind and other potential causes of contamination or loss of sample. Inspect the train before and during disassembly and note any abnormal conditions. The sample is recovered and treated as follows (see schematic in Figure 3.1-2). Ensure that all items necessary for recovery of the sample do not contaminate it.

3.1.5.2.1 Container No. 1 (Filter). Carefully remove the filter from the filter holder and place it in its identified petri dish container. Acid-washed polypropylene or Teflon coated tweezers or clean, disposable surgical gloves rinsed with water and dried should be used to handle the filters. If it is necessary to fold the filter, make certain the particulate cake is inside the fold. Carefully transfer the filter and any particulate matter or filter fibers that adhere to the filter holder gasket to the petri dish by using a dry (acid-cleaned) nylon bristle brush. Do not use any metal-containing materials when recovering this train. Seal the labeled petri dish.



* Number in parentheses indicates container number

Figure 3.1-2 Sample recovery scheme.

3.1.5.2.2 Container No. 2 (Acetone Rinse). NOTE: Perform Section 3.1.5.2.2 only if determination of particulate emissions are desired in addition to metals emissions. If only metals emissions are desired, skip Section 3.1.5.2.2 and go to Section 3.1.5.2.3. Taking care to see that dust on the outside of the probe or other exterior surfaces does not get into the sample, quantitatively recover particulate matter and any condensate from the probe nozzle, probe fitting (plastic such as Teflon, polypropylene, etc. fittings are recommended to prevent contamination by metal fittings; further, if desired, a single glass piece consisting of a combined probe tip and probe liner may be used, but such a single glass piece is not a requirement of this methodology), probe liner, and front half of the filter holder by washing these components with 100 ml of acetone and placing the wash in a glass container. Note: The use of exactly 100 ml is necessary for the subsequent blank correction procedures. Distilled water may be used instead of acetone when approved by the Administrator and shall be used when specified by the Administrator; in these cases, save a water blank and follow the Administrator's directions on analysis. Perform the acetone rinses as follows: Carefully remove the probe nozzle and clean the inside surface by rinsing with acetone from a wash bottle and brushing with a nonmetallic brush. Brush until the acetone rinse shows no visible particles, after which make a final rinse of the inside surface with acetone.

Brush and rinse the sample-exposed, inside parts of the fitting with acetone in a similar way until no visible particles remain.

Rinse the probe liner with acetone by tilting and rotating the probe while squirting acetone into its upper end so that all inside surfaces will be wetted with acetone. Allow the acetone to drain from the lower end into the sample container. A funnel may be used to aid in transferring liquid washings to the container. Follow the acetone rinse with a nonmetallic probe brush. Hold the probe in an inclined position, squirt acetone into the upper end as the probe brush is being pushed with a twisting action through the probe; hold a sample container underneath the lower end of the probe, and catch any acetone and particulate matter which is brushed through the probe three times or more until none remains in the probe liner on visual inspection. Rinse the

brush with acetone, and quantitatively collect these washings in the sample container. After the brushing, make a final acetone rinse of the probe as described above.

It is recommended that two people clean the probe to minimize sample losses. Between sampling runs, keep brushes clean and protected from contamination.

Clean the inside of the front half of the filter holder by rubbing the surfaces with a nonmetallic nylon bristle brush and rinsing with acetone. Rinse each surface three times or more if needed to remove visible particulate. Make a final rinse of the brush and filter holder. After all acetone washings and particulate matter have been collected in the sample container, tighten the lid on the sample container so that acetone will not leak out when it is shipped to the laboratory. Mark the height of the fluid level to determine whether or not leakage occurred during transport. Label the container clearly to identify its contents.

3.1.5.2.3 Container No. 3 (Probe Rinse). Keep the probe assembly clean and free from contamination as described in Section 3.1.5.2.2 of this method during the 0.1 N nitric acid rinse described below. Rinse the probe nozzle and fitting probe liner, and front half of the filter holder thoroughly with 100 ml of 0.1 N nitric acid and place the wash into a sample storage container. Note: The use of exactly 100 ml is necessary for the subsequent blank correction procedures. Perform the rinses as applicable and generally as described in Method 12, Section 5.2.2. Record the volume of the combined rinse. Mark the height of the fluid level on the outside of the storage container and use this mark to determine if leakage occurs during transport. Seal the container and clearly label the contents. Finally, rinse the nozzle, probe liner, and front half of the filter holder with water followed by acetone and discard these rinses.

3.1.5.2.4 Container No. 4 (Impingers 1 through 3, $\text{HNO}_3/\text{H}_2\text{O}_2$ Impingers and Moisture Knockout Impinger, when used, Contents and Rinses). Due to the potentially large quantity of liquid involved, the tester may place

the impinger solutions from impingers 1 through 3 in more than one container. Measure the liquid in the first three impingers volumetrically to within 0.5 ml using a graduated cylinder. Record the volume of liquid present. This information is required to calculate the moisture content of the sampled flue gas. Clean each of the first three impingers, the filter support, the back half of the filter housing, and connecting glassware by thoroughly rinsing with 100 ml of 0.1 N nitric acid using the procedure as applicable and generally as described in Method 12, Section 5.2.4. Note: The use of exactly 100 ml of 0.1 N nitric acid rinse is necessary for the subsequent blank correction procedures. Combine the rinses and impinger solutions, measure and record the volume. Mark the height of the fluid level on the outside of the container to determine if leakage occurs during transport. Seal the container and clearly label the contents.

3.1.5.2.5 Container Nos. 5A, 5B, and 5C. 5A (0.1 N HNO_3), 5B ($\text{KMnO}_4/\text{H}_2\text{SO}_4$ absorbing solution), and 5C (8 N HCl rinse and dilution). (As described previously at the end of Section 3.1.3.1.5 of this method, if mercury is not being measured in this train, then impingers 4, 5, and 6, as shown in Figure A-1, are not necessary and may be eliminated.) Pour all the liquid, if any, from the impinger which was empty at the start of the run and which immediately precedes the two permanganate impingers (normally impinger No. 4) into a graduated cylinder and measure the volume to within 0.5 ml. This information is required to calculate the moisture content of the sampled flue gas. Place the liquid in Sample Container No. 5A. Rinse the impinger (No. 4) with 100 ml of 0.1 N HNO_3 and place this into Container No. 5A.

Pour all the liquid from the two permanganate impingers into a graduated cylinder and measure the volume to within 0.5 ml. This information is required to calculate the moisture content of the sampled flue gas. Place this KMnO_4 absorbing solution stack sample from the two permanganate impingers into Container No. 5B. Using 100 ml total of fresh acidified potassium permanganate solution, rinse the two permanganate impingers and connecting glass pieces a minimum of three times and place the rinses into Container No. 5B, carefully ensuring transfer of all loose precipitated materials from the two impingers into Container No. 5B. Using 100 ml total of water, rinse the

permanganate impingers and connecting glass pieces a minimum of three times, and place the rinses into Container 5B, carefully ensuring transfer of all loose precipitated material, if any, from the two impingers into Container No. 5B. Mark the height of the fluid level on the outside of the bottle to determine if leakage occurs during transport. See the following note and the Precaution in Paragraph 3.1.4.2.2 and properly prepare the bottle and clearly label the contents.

Note: Due to the potential reaction of the potassium permanganate with the acid, there may be pressure buildup in the sample storage bottles. These bottles shall not be completely filled and shall be vented to relieve potential excess pressure. Venting is required. A No. 70-72 hole drilled in the container cap and Teflon liner has been used.

If no visible deposits remain after the above described water rinse, do not rinse with 8 N HCl. However, if deposits do remain on the glassware after this water rinse, wash the impinger surfaces with 25 ml of 8 N HCl, and place the wash in a separate sample container labeled Container No. 5C containing 200 ml of water as follows: Place 200 ml of water in a sample container labeled Container No. 5C. Wash the impinger walls and stem with the HCl by turning the impinger on its side and rotating it so that the HCl contacts all inside surfaces. Use a total of only 25 ml of 8 N HCl for rinsing both permanganate impingers combined. Rinse the first impinger, then pour the actual rinse used for the first impinger into the second impinger for its rinse. Finally, pour the 25 ml of 8 N HCl rinse carefully with stirring into Container No. 5C. Mark the height of the fluid level on the outside of the bottle to determine if leakage occurs during transport.

3.1.5.2.6 Container No. 6 (Silica Gel). Note the color of the indicating silica gel to determine whether it has been completely spent and make a notation of its condition. Transfer the silica gel from its impinger to its original container and seal. The tester may use a funnel to pour the silica gel and a rubber policeman to remove the silica gel from the impinger.

The small amount of particles that may adhere to the impinger wall need not be removed. Do not use water or other liquids to transfer the silica gel since weight gained in the silica gel impinger is used for moisture calculations. Alternatively, if a balance is available in the field, record the weight of the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g.

3.1.5.2.7 Container No. 7 (Acetone Blank). If particulate emissions are to be determined, at least once during each field test, place a 100-ml portion of the acetone used in the sample recovery process into a labeled container for use in the front-half field reagent blank. Seal the container.

3.1.5.2.8 Container No. 8A (0.1 N Nitric Acid Blank). At least once during each field test, place 300 ml of the 0.1 N nitric acid solution used in the sample recovery process into a labeled container for use in the front-half and back-half field reagent blanks. Seal the container. Container No. 8B (water blank). At least once during each field test, place 100 ml of the water used in the sample recovery process into a labeled Container No. 8B. Seal the container.

3.1.5.2.9 Container No. 9 (5% Nitric Acid/10% Hydrogen Peroxide Blank). At least once during each field test, place 200 ml of the 5% nitric acid/10% hydrogen peroxide solution used as the nitric acid impinger reagent into a labeled container for use in the back-half field reagent blank. Seal the container.

3.1.5.2.10 Container No. 10 (Acidified Potassium Permanganate Blank). At least once during each field test, place 100 ml of the acidified potassium permanganate solution used as the impinger solution and in the sample recovery process into a labeled container for use in the back-half field reagent blank for mercury analysis. Prepare the container as described in Section 3.1.5.2.5.

Note: Due to the potential reaction of the potassium permanganate with the acid, there may be pressure buildup in the sample storage bottles. These bottles shall not be

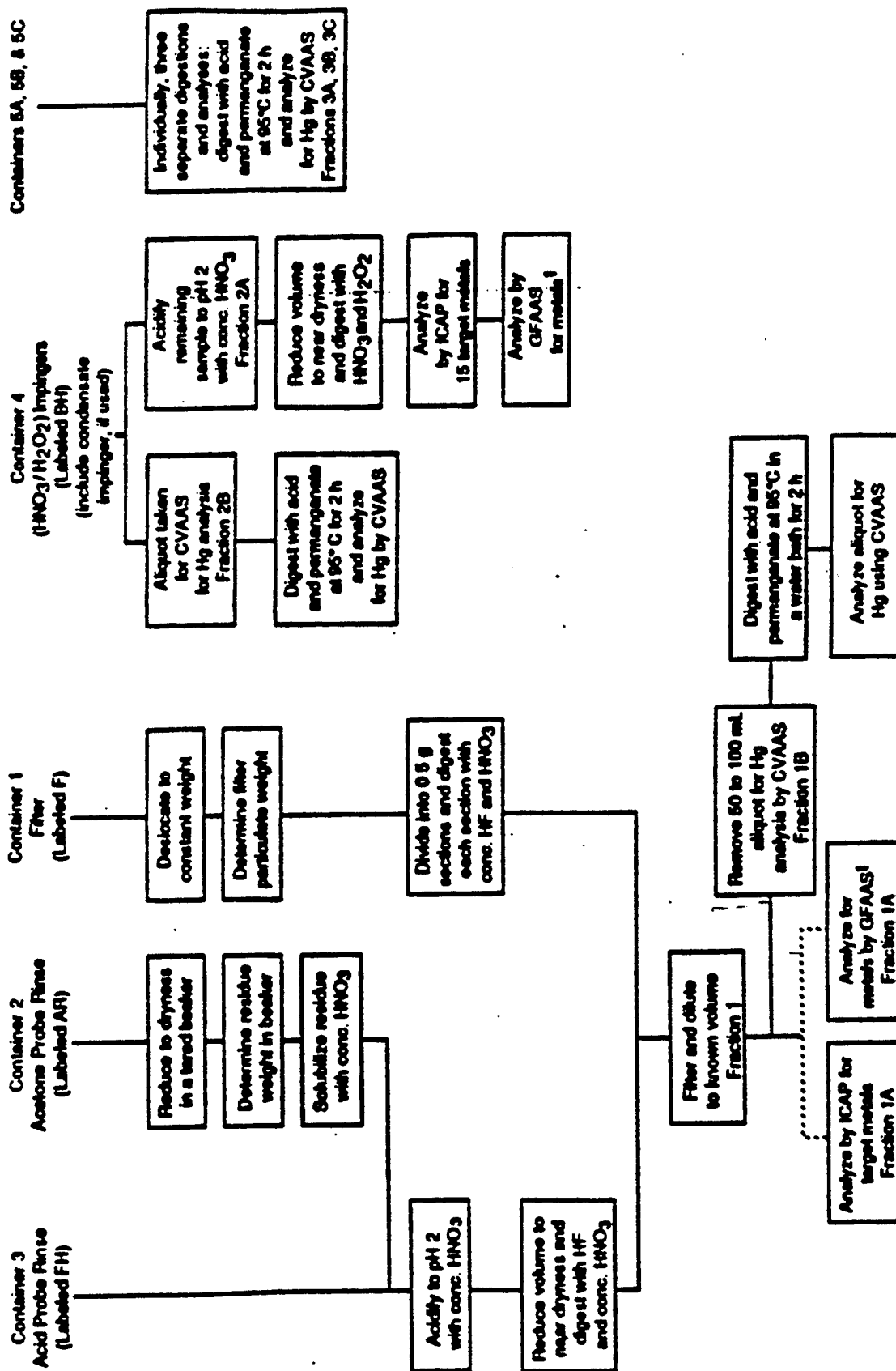
completely filled and shall be vented to relieve potential excess pressure. Venting is required. A No. 70-72 hole drilled in the container cap and Teflon liner has been used.

3.1.5.2.11 Container No. 11 (8 N HCl Blank). At least once during each field test, perform both of the following: Place 200 ml of water into a sample container. Pour 25 ml of 8 N HCl carefully with stirring into the 200 ml of water in the container. Mix well and seal the container.

3.1.5.2.12 Container No. 12 (Filter Blank). Once during each field test, place three unused blank filters from the same lot as the sampling filters in a labeled petri dish. Seal the petri dish. These will be used in the front-half field reagent blank.

3.1.5.3 Sample Preparation. Note the level of the liquid in each of the containers and determine if any sample was lost during shipment. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results. A diagram illustrating sample preparation and analysis procedures for each of the sample train components is shown in Figure 3.1-3.

3.1.5.3.1 Container No. 1 (Filter). If particulate emissions are being determined, then desiccate the filter and filter catch without added heat and weigh to a constant weight as described in Section 4.3 of Method 5. For analysis of metals, divide the filter with its filter catch into portions containing approximately 0.5 g each and place into the analyst's choice of either individual microwave pressure relief vessels or Parr¹ Bombs. Add 6 ml of concentrated nitric acid and 4 ml of concentrated hydrofluoric acid to each vessel. For microwave heating, microwave the sample vessels for approximately 12-15 minutes in intervals of 1 to 2 minutes at 600 Watts. For conventional heating, heat the Parr Bombs at 140°C (285°F) for 6 hours. Cool the samples to room temperature and combine with the acid digested probe rinse as required in Section 3.1.5.3.3, below.



¹ Analysis by AAS for metals found at less than 2 ug/mL in digestate solution, if desired. Or analyze for each metal by AAS, if desired.

Figure 3.1-3 Sample preparation and analysis scheme.

- Notes:
1. Suggested microwave heating times are approximate and are dependent upon the number of samples being digested. Twelve to 15 minute heating times have been found to be acceptable for simultaneous digestion of up to 12 individual samples. Sufficient heating is evidenced by sorbent reflux within the vessel.
 2. If the sampling train uses an optional cyclone, the cyclone catch should be prepared and digested using the same procedures described for the filters and combined with the digested filter samples.

3.1.5.3.2 Container No. 2 (Acetone Rinse). Note the level of liquid in the container and confirm on the analysis sheet whether leakage occurred during transport. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results. Measure the liquid in this container either volumetrically to ± 1 ml or gravimetrically to ± 0.5 g. Transfer the contents to an acid-cleaned, tared 250-ml beaker and evaporate to dryness at ambient temperature and pressure. If particulate emissions are being determined, desiccate for 24 hours without added heat, weigh to a constant weight according to the procedures described in Section 4.3 of Method 5, and report the results to the nearest 0.1 mg. Redissolve the residue with 10 ml of concentrated nitric acid and, carefully with stirring, quantitatively combine the resultant sample including all liquid and any particulate matter with Container No. 3 prior to beginning the following Section 3.1.5.3.3.

3.1.5.3.3 Container No. 3 (Probe Rinse). The pH of this sample shall be 2 or lower. If the pH is higher, the sample should be acidified to pH 2 by the careful addition with stirring of concentrated nitric acid. The sample should be rinsed into a beaker with water and the beaker should be covered with a ribbed watchglass. The sample volume should be reduced to approximately 20 ml by heating on a hot plate at a temperature just below boiling. Digest the sample in microwave vessels or Parr[®] Bombs by quantitatively transferring the sample to the vessel or bomb, by carefully adding the 6 ml of concentrated nitric acid and 4 ml of concentrated hydrofluoric acid

and then continuing to follow the procedures described in Section 3.1.5.3.1; then combine the resultant sample directly with the acid digested portions of the filter prepared previously in Section 3.1.5.3.1. The resultant combined sample is referred to as Fraction 1 precursor. Filter the combined solution of the acid digested filter and probe rinse samples using Whatman 541 filter paper. Dilute to 300 ml (or the appropriate volume for the expected metals concentration) with water. This dilution is Fraction 1. Measure and record the volume of the Fraction 1 solution to within 0.1 ml. Quantitatively remove a 50-ml aliquot and label as Fraction 1B. Label the remaining 250-ml portion as Fraction 1A. Fraction 1A is used for ICAP or AAS analysis. Fraction 1B is used for the determination of front-half mercury.

3.1.5.3.4 Container No. 4 (Impingers 1-3). Measure and record the total volume of this sample (Fraction 2) to within 0.5 ml. Remove a 75- to 100-ml aliquot for mercury analysis and label as Fraction 2B. Label the remaining portion of Container No. 4 as aliquot Fraction 2A. Aliquot Fraction 2A defines the volume of 2A prior to digestion. All of the aliquot Fraction 2A is digested to produce concentrated Fraction 2A. Concentrated Fraction 2A defines the volume of 2A after digestion which is normally 150 ml. Only concentrated Fraction 2A is analyzed for metals (except that it is not analyzed for mercury). The Fraction 2B aliquot should be prepared and analyzed for mercury as described in Section 3.1.5.4.3. Aliquot Fraction 2A shall be pH 2 or lower. If necessary, use concentrated nitric acid, by careful addition and stirring, to lower aliquot Fraction 2A to pH 2. The sample should be rinsed into a beaker with water and the beaker should be covered with a ribbed watchglass. The sample volume should be reduced to approximately 20 ml by heating on a hot plate at a temperature just below boiling. Next follow either the conventional or microwave digestion procedures described in Sections 3.1.5.3.4.1 and 3.1.5.3.4.2, below.

3.1.5.3.4.1 Conventional Digestion Procedure. Add 30 ml of 50 percent nitric acid and heat for 30 minutes on a hot plate to just below boiling. Add 10 ml of 3 percent hydrogen peroxide and heat for 20 more minutes. Add 50 ml of hot water and heat the sample for an additional 20 minutes. Cool, filter the sample, and dilute to 150 ml (or the appropriate

volume for the expected metals concentrations) with water. This dilution is concentrated Fraction 2A. Measure and record the volume of the Fraction 2A solution to within 0.1 ml.

3.1.5.3.4.2 Microwave Digestion Procedure. Add 10 ml of 50 percent nitric acid and heat for 6 minutes in intervals of 1 to 2 minutes at 600 Watts. Allow the sample to cool. Add 10 ml of 3 percent hydrogen peroxide and heat for 2 more minutes. Add 50 ml of hot water and heat for an additional 5 minutes. Cool, filter the sample, and dilute to 150 ml (or the appropriate volume for the expected metals concentrations) with water. This dilution is concentrated Fraction 2A. Measure and record the volume of the Fraction 2A solution to within 0.1 ml.

Note: All microwave heating times given are approximate and are dependent upon the number of samples being digested at a time. Heating times as given above have been found acceptable for simultaneous digestion of up to 12 individual samples. Sufficient heating is evidenced by solvent reflux within the vessel.

3.1.5.3.5 Container Nos. 5A, 5B, and 5C (Impingers 4, 5, and 6). Keep these samples separate from each other and measure and record the volumes of 5A and 5B separately to within 0.5 ml. Dilute sample 5C to 500 ml with water. These samples 5A, 5B, and 5C are referred to respectively as Fractions 3A, 3B, and 3C. Follow the analysis procedures described in Section 3.1.5.4.3.

Because the permanganate rinse and water rinse have the capability to recover a high percentage of the mercury from the permanganate impingers, the amount of mercury in the HCl rinse (Fraction 3C) may be very small, possibly even insignificantly small. However, as instructed in this method, add the total of any mercury measured in and calculated for the HCl rinse (Fraction 3C) to that for Fractions 1B, 2B, 3A, and 3B for calculation of the total sample mercury concentration.

3.1.5.3.6 Container No. 6 (Silica Gel). Weigh the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g using a balance. (This step may be conducted in the field:)

3.1.5.4 Sample Analysis. For each sampling train, seven individual samples are generated for analysis. A schematic identifying each sample and the prescribed sample preparation and analysis scheme is shown in Figure 3.1-3. The first two samples, labeled Fractions 1A and 1B, consist of the digested samples from the front half of the train. Fraction 1A is for ICAP or AAS analysis as described in Sections 3.1.5.4.1 and/or 3.1.5.4.2. Fraction 1B is for determination of front-half mercury as described in Section 3.1.5.4.3.

The back half of the train was used to prepare the third through seventh samples. The third and fourth samples, labeled Fractions 2A and 2B, contain the digested samples from the moisture knockout, if used, and $\text{HNO}_3/\text{H}_2\text{O}_2$ Impingers 1 through 3. Fraction 2A is for ICAP or AAS analysis. Fraction 2B will be analyzed for mercury.

The fifth through seventh samples, labeled Fractions 3A, 3B, and 3C, consist of the impinger contents and rinses from the empty and permanganate impingers 4, 5, and 6. These samples are analyzed for mercury as described in Section 3.1.5.4.3. The total back-half mercury catch is determined from the sum of Fraction 2B and Fractions 3A, 3B, and 3C.

3.1.5.4.1 ICAP Analysis. Fraction 1A and Fraction 2A are analyzed by ICAP using EPA SW-846 Method 6010 or Method 200.7 (40 CFR 136, Appendix C). Calibrate the ICAP, and set up an analysis program as described in Method 6010 or Method 200.7. The quality control procedures described in Section 3.1.7.3.1 of this method shall be followed. Recommended wavelengths for use in the analysis are listed below:

Element	Wavelength (nm)
Aluminum	308.215
Antimony	206.833
Arsenic	193.696
Barium	455.403
Beryllium	313.042
Cadmium	226.502
Chromium	267.716
Copper	324.754
Iron	259.940
Lead	220.353
Manganese	257.610
Nickel	231.604
Phosphorus	214.914
Selenium	196.026
Silver	328.068
Thallium	190.864
Zinc	213.856

The wavelengths listed are recommended because of their sensitivity and overall acceptance. Other wavelengths may be substituted if they can provide the needed sensitivity and are treated with the same corrective techniques for spectral interference.

Initially, analyze all samples for the desired target metals (except mercury) plus iron and aluminum. If iron and aluminum are present in the sample, the sample may have to be diluted so that each of these elements is at a concentration of less than 50 ppm to reduce their spectral interferences on arsenic, cadmium, chromium, and lead.

Note: When analyzing samples in a hydrofluoric acid matrix, an alumina torch should be used; since all front-half samples will contain hydrofluoric acid, use an alumina torch.

3.1.5.4.2 AAS by Direct Aspiration and/or Graphite Furnace. If analysis of metals in Fraction 1A and Fraction 2A using graphite furnace or direct aspiration AAS is desired, Table 3.1-2 should be used to determine

Table 3.1-2

APPLICABLE TECHNIQUES, METHODS, AND MINIMIZATION OF INTERFERENCE FOR AAS ANALYSIS

Metal	Technique	SW-846 Method No.	Wavelength (nm)	Cause	Interferences	Minimization
Sb	Aspiration	7040	217.6	1000 mg/mL Pb Ni, Cu, or acid		Use secondary wavelength of 231.1 nm; match sample & standards' acid concentration or use nitrous oxide/acetylene flame
Sb	Furnace	7041	217.6	High Pb		Secondary wavelength or Zeeman correction
As	Furnace	7060	193.7	Arsenic volatilization		Spiked samples and add nickel nitrate solution to digestates prior to analysis
				Aluminum		Use Zeeman background correction
Ba	Aspiration	7080	553.6	Calcium		High hollow cathode current and narrow band set
				Barium ionization		2 mL of KCl per 100 mL of sample
Be	Aspiration	7090	234.9	500 ppm Al		Add 0.1% fluoride
Be	Furnace	7091	234.9	High Mg and Si		Use method of standard additions
Cd	Aspiration	7130	228.8	Be in optical path		Optimize parameters to minimize effects
				Absorption and light scattering		Background correction is required
Cd	Furnace	7131	228.8	As above		As above
				Excess chloride		Ammonium phosphate used as a matrix modifier
				Pipet tips		Use cadmium-free tips
Cr	Aspiration	7190	357.9	Alkali metal		KCl ionization suppressant in samples and standards
				Absorption and scatter		Consult manufacturer's literature
Cr	Furnace	7191	357.9	200 mg/L Ca and P		All calcium nitrate for a known constant effect and to eliminate effect of phosphate
Cu	Aspiration	7210	324.7	Absorption and scatter		Consult manufacturer's manual

(continued)

Table 3.1-2

APPLICABLE TECHNIQUES, METHODS, AND MINIMIZATION OF INTERFERENCE FOR AAS ANALYSIS

Metal	Technique	SW-846 Method No.	Wavelength (nm)	Cause	Interferences	Minimization
Fe	Aspiration	7380	248.3	Contamination		Great care taken to avoid contamination
Pb	Aspiration	7420	283.3	217.0 nm alternate		Background correction required
Pb	Furnace	7421	283.3	Poor recoveries		Matrix modifier, add 10 uL of phosphorus acid to 1 mL of prepared sample in sampler cup
Mn	Aspiration	7460	279.5	403.1 nm alternate		Background correction required
Ni	Aspiration	7520	232.0	352.4 nm alternate Fe, Co, and Cr		Background correction required Matrix matching or nitrous-oxide/acetylene flame
Se	Furnace	7740	196.0	Nonlinear response Volatility		Sample dilution or use 352.3 nm line Spike samples and reference materials and add nickel nitrate to minimize volatilization
Ag	Aspiration	7760	328.1	Adsorption & scatter Adsorption & scatter AgCl insoluble Viscosity		Background correction is required and Zeeman background correction can be useful Background correction is required Avoid hydrochloric acid unless silver is in solution as a chloride complex Sample and standards monitored for aspiration rate
Tl	Aspiration	7840	276.8			Background correction is required Hydrochloric acid should not be used
Tl	Furnace	7841	276.8	Hydrochloric acid or chloride		Background correction is required Verify that losses are not occurring for volatilization by spiked samples or standard addition; Palladium is a suitable matrix modifier
Zn	Aspiration	7950	213.9	High Si, Cu, & P Contamination		Strontium removes Cu and phosphate Great care taken to avoid contamination

which techniques and methods should be applied for each target metal. Table 3.1-2 should also be consulted to determine possible interferences and techniques to be followed for their minimization. Calibrate the instrument according to Section 3.1.6.3 and follow the quality control procedures specified in Section 3.1.7.3.2.

3.1.5.4.3 Cold Vapor AAS Mercury Analysis. Fraction 1B, Fraction 2B, and Fractions 3A, 3B, and 3C should be analyzed separately for mercury using cold vapor atomic absorption spectroscopy following the method outlined in EPA SW-846 Method 7470 or in Standard Methods for Water and Wastewater Analysis, 15th Edition, Method 303F. Set up the calibration curve (zero to 1000 ng) as described in SW-846 Method 7470 or similar to Method 303F, using 300-ml BOD bottles instead of Erlenmeyers. Dilute separately, as described below, a 1 ml to 10 ml aliquot of each original sample to 100 ml with water. Record the amount of the aliquot used for dilution to 100 ml. If no prior knowledge exists of the expected amount of mercury in the sample, a 5-ml aliquot is suggested for the first dilution to 100 ml and analysis. To determine the stack emission value for mercury, the amount of the aliquot of the sample used for dilution and analysis is dependent on the amount of mercury in the aliquot: the total amount of mercury in the aliquot used for analysis shall be less than 1 μg , and within the range (zero to 1000 ng) of the calibration curve. Place each sample aliquot into a separate 300-ml BOD bottle and add enough Type II water to make a total volume of 100 ml. Then analyze the 100 ml for mercury by adding to it sequentially the sample preparation solutions and performing the sample preparation and analysis as described in the procedures of SW-846 Method 7470 or Method 303F. If, during the described analysis, the reading maximum(s) are off-scale (because the aliquot of the original sample analyzed contained more mercury than the maximum of the calibration range) including the analysis of the 100-ml dilution of the 1-ml aliquot of the original sample causing a reading maximum which is off-scale, then perform the following: dilute the original sample (or a portion of it) with 0.15% HNO_3 in water (1.5 ml concentrated HNO_3 per liter aqueous solution) so that when a 1-ml to 10-ml aliquot of the dilution of the original sample is then further diluted to 100 ml in the BOD bottle,

and analyzed by the procedures described above, it will yield an analysis within the range of the calibration curve.

3.1.6 Calibration

Maintain a laboratory log of all calibrations.

3.1.6.1 Sampling Train Calibration. Calibrate the sampling train components according to the indicated sections of Method 5: Probe Nozzle (Section 5.1); Pitot Tube (Section 5.2); Metering System (Section 5.3); Probe Heater (Section 5.4); Temperature Gauges (Section 5.5); Leak-Check of the Metering System (Section 5.6); and Barometer (Section 5.7).

3.1.6.2 Inductively Coupled Argon Plasma Spectrometer Calibration. Prepare standards as outlined in Section 3.1.4.4. Profile and calibrate the instrument according to the instrument manufacturer's recommended procedures using the above standards. The instrument calibration should be checked once per hour. If the instrument does not reproduce the concentrations of the standard within 10 percent, the complete calibration procedures should be performed.

3.1.6.3 Atomic Absorption Spectrometer - Direct Aspiration, Graphite Furnace and Cold Vapor Mercury Analyses. Prepare the standards as outlined in Section 3.1.4.4. Calibrate the spectrometer using these prepared standards. Calibration procedures are also outlined in the EPA methods referred to in Table 3.1-2 and in SW-846 Method 7470 or Standard Methods for Water and Wastewater, 15th Edition, Method 303F (for mercury). Each standard curve should be run in duplicate and the mean values used to calculate the calibration line. The instrument should be recalibrated approximately once every 10 to 12 samples.

3.1.7 Quality Control

3.1.7.1 Sampling. Field Reagent Blanks. When analyzed, the blank samples in Container Numbers 7 through 12 produced previously in Sections

3.1.5.2.7 through 3.1.5.2.12, respectively, shall be processed, digested, and analyzed as follows: Digest and process one of the filters from Container No. 12 per Section 3.1.5.3.1, 100 ml from Container No. 7 per Section 3.1.5.3.2, and 100 ml from Container No. 8A per Section 3.1.5.3.3. This produces Fraction Blank 1A and Fraction Blank 1B from Fraction Blank 1. [If desired, the other two filters may be digested separately according to Section 3.1.5.3.1, diluted separately to 300 ml each, and analyzed separately to produce a blank value for each of the two additional filters. If these analyses are performed, they will produce two additional values for each of Fraction Blank 1A and Fraction Blank 1B. The three Fraction Blank 1A values will be calculated as three values of M_{mb} in Equation 3 of Section 3.1.8.4.3, and then the three values shall be totalled and divided by 3 to become the value M_{mb} to be used in the computation of M_t by Equation 3. Similarly, the three Fraction Blank 1B values will be calculated separately as three values, totalled, averaged, and used as the value for Hg_{mb} in Equation 8 of Section 3.1.8.5.3. The analyses of the two extra filters are optional and are not a requirement of this method, but if the analyses are performed, the results must be considered as described above.] Combine 100 ml of Container No. 8A with 200 ml of the contents of Container No. 9 and digest and process the resultant volume per Section 3.1.5.3.4. This produces concentrated Fraction Blank 2A and Fraction Blank 2B from Fraction Blank 2. A 100-ml portion of Container No. 8A is Fraction Blank 3A. Combine 100 ml of the contents of Container No. 10 with 33 ml of the contents of Container No. 8B. This produces Fraction Blank 3B (use 400 ml as the volume of Fraction Blank 3B when calculating the blank value. Use the actual volumes when calculating all the other blank values). Dilute 225 ml of the contents of Container No. 11 to 500 ml with water. This produces Fraction Blank 3C. Analyze Fraction Blank 1A and Fraction Blank 2A per Section 3.1.5.4.1 and/or 3.1.5.4.2. Analyze Fraction Blank 1B, Fraction Blank 2B, and Fraction Blanks 3A, 3B, and 3C per Section 3.1.5.4.3. The analysis of Fraction Blank 1A produces the front-half reagent blank correction values for the metals except mercury; the analysis of Fraction Blank 1B produces the front-half reagent blank correction value for mercury. The analysis of concentrated Fraction Blank 2A produces the back-half reagent blank correction values for the metals except mercury, while

separate analysis of Fraction Blanks 2B, 3A, 3B, and 3C produce the back-half reagent blank correction value for mercury.

3.1.7.2 An attempt may be made to determine if the laboratory reagents used in Section 3.1.5.3 caused contamination. They should be analyzed by the procedures in Section 3.1.5.4. The Administrator will determine whether the laboratory blank reagent values can be used in the calculation of the stationary source test results.

3.1.7.3 ~~Quality Control Samples.~~ The following quality control samples should be analyzed.

3.1.7.3.1 ICAP Analysis. Follow the quality control shown in Section 8 of Method 6010. For the purposes of a three-run test series, these requirements have been modified to include the following: two instrument check standard runs, two calibration blank runs, one interference check sample at the beginning of the analysis (must be within 25% or analyze by the method of standard additions), one quality control sample to check the accuracy of the calibration standards (must be within 25% of calibration), and one duplicate analysis (must be within 10% of average or repeat all analyses).

3.1.7.3.2 Direct Aspiration and/or Graphite Furnace AAS Analysis for antimony, arsenic, barium, beryllium, cadmium, copper, chromium, lead, nickel, manganese, mercury, phosphorus, selenium, silver, thallium, and zinc. All samples should be analyzed in duplicate. Perform a matrix spike on at least one front-half sample and one back-half sample or one combined sample. If recoveries of less than 75 percent or greater than 125 percent are obtained for the matrix spike, analyze each sample by the method of standard additions. A quality control sample should be analyzed to check the accuracy of the calibration standards. The results must be within 10% or the calibration repeated.

3.1.7.3.3 Cold Vapor AAS Analysis for Mercury. All samples should be analyzed in duplicate. A quality control sample should be analyzed to check the accuracy of the calibration standards (within 15% or repeat

calibration). Perform a matrix spike on one sample from the nitric impinger portion (must be within 25% or samples must be analyzed by the method of standard additions). Additional information on quality control can be obtained from EPA SW-846 Method 7470 or in Standard Methods for the Examination of Water and Wastewater, 15th Edition, Method 303F.

3.1.8 Calculations

3.1.8.1 Dry Gas Volume. Using the data from this test, calculate $V_{m(std)}$, the dry gas sample volume at standard conditions as outlined in Section 6.3 of Method-5.

3.1.8.2 Volume of Water Vapor and Moisture Content. Using the data obtained from this test, calculate the volume of water vapor $V_{w(std)}$ and the moisture content B_{ws} of the stack gas. Use Equations 5-2 and 5-3 of Method 5.

3.1.8.3 Stack Gas Velocity. Using the data from this test and Equation 2-9 of Method 2, calculate the average stack gas velocity.

3.1.8.4 Metals (Except Mercury) in Source Sample.

3.1.8.4.1 Fraction 1A, Front Half, Metals (except Hg). Calculate separately the amount of each metal collected in Fraction 1 of the sampling train using the following equation:

$$M_{th} = C_{a1} F_d V_{soln,1} \quad \text{Eq. 1}^*$$

where:

M_{th} = total mass of each metal (except Hg) collected in the front half of the sampling train (Fraction 1), μg .

C_{a1} = concentration of metal in sample Fraction 1A as read from the standard curve ($\mu\text{g/ml}$).

*If Fractions 1A and 2A are combined, proportional aliquots must be used. Appropriate changes must be made in Equations 1-3 to reflect this approach.

F_d = dilution factor (F_d = the inverse of the fractional portion of the concentrated sample in the solution actually used in the instrument to produce the reading C_{a1} . For example, when 2 ml of Fraction 1A are diluted to 10 ml, $F_d = 5$).

$V_{soln,1}$ = total volume of digested sample solution (Fraction 1), ml.

3.1.8.4.2 Fraction 2A, Back Half, Metals (except Hg). Calculate separately the amount of each metal collected in Fraction 2 of the sampling train using the following equation:

$$M_{bh} = C_{a2} F_a V_a \quad \text{Eq. 2*}$$

where:

M_{bh} = total mass of each metal (except Hg) collected in the back half of the sampling train (Fraction 2), μg .

C_{a2} = concentration of metal in sample concentrated Fraction 2A, as read from the standard curve ($\mu\text{g/ml}$).

F_a = aliquot factor, volume of Fraction 2 divided by volume of aliquot Fraction 2A (see Section 3.1.5.3.4).

V_a = total volume of digested sample solution (concentrated Fraction 2A), ml (see Section 3.1.5.3.4.1 or 3.1.5.3.4.2, as applicable).

3.1.8.4.3 Total Train, Metals (except Hg). Calculate the total amount of each of the quantified metals collected in the sampling train as follows:

$$M_t = (M_{th} - M_{thb}) + (M_{bh} - M_{bbh}) \quad \text{Eq. 3*}$$

where:

M_t = total mass of each metal (separately stated for each metal) collected in the sampling train, μg .

M_{thb} = blank correction value for mass of metal detected in front-half field reagent blank, μg .

M_{bbh} = blank correction value for mass of metal detected in back-half field reagent blank, μg .

Note: If the measured blank value for the front half (M_{thb}) is in the range 0.0 to A μg [where A μg equals the value determined by multiplying 1.4 μg per square inch (1.4 $\mu\text{g/in}^2$) times the actual area in square inches (in^2)

of the filter used in the emission sample], m_{thb} may be used to correct the emission sample value (m_{th}); if m_{thb} exceeds $A \mu g$, the greater of the two following values (either I. or II.) may be used:

- I. $A \mu g$, or
- II. the lesser of (a) m_{thb} , or (b) 5 percent of m_{th} .

If the measured blank value for the back half (m_{bbb}) is in the range of 0.0 to $1 \mu g$, m_{bbb} may be used to correct the emission sample value (m_{bh}); if m_{bbb} exceeds $1 \mu g$, the greater of the two following values may be used: $1 \mu g$ or 5 percent of m_{bh} .

3.1.8.5 Mercury in Source Sample.

3.1.8.5.1 Fraction 1B, Front Half, Hg. Calculate the amount of mercury collected in the front half, Fraction 1, of the sampling train using the following equation:

$$Hg_{th} = \frac{Q_{th}}{V_{f1B}} \times V_{soln,1} \quad \text{Eq. 4}$$

where:

- Hg_{th} = total mass of mercury collected in the front half of the sampling train (Fraction 1), μg .
- Q_{th} = quantity of mercury in analyzed sample, μg .
- $V_{soln,1}$ = total volume of digested sample solution (Fraction 1), ml.
- V_{f1B} = volume of Fraction 1B analyzed, ml. See the following notice.

Note: V_{f1B} is the actual amount of Fraction 1B analyzed. For example, if 1 ml of Fraction 1B were diluted to 100 ml to bring it into the proper analytical range, and 1 ml of the 100-ml dilution were analyzed, V_{f1B} would be 0.01 ml.

3.1.8.5.2 Fraction 2B and Fractions 3A, 3B, and 3C, Back Half, Hg. Calculate the amount of mercury collected in Fractions 2 using Equation 5 and in Fractions 3A, 3B, and 3C using Equation 6. Calculate the total amount of mercury collected in the back half of the sampling train using Equation 7.

$$Hg_{bh2} = \frac{Q_{bh2}}{V_{f2B}} \times V_{soln,2} \quad \text{Eq. 5}$$

where:

- Hg_{bh2} = total mass of mercury collected in Fraction 2, μg .
- Q_{bh2} = quantity of mercury in analyzed sample, μg .
- $V_{soln,2}$ = total volume of Fraction 2, ml.
- V_{f2B} = volume of Fraction 2B analyzed, ml (see the following note).

Note: V_{f2B} is the actual amount of Fraction 2B analyzed. For example, if 1 ml of Fraction 2B were diluted to 10 ml to bring it into the proper analytical range, and 5 ml of the 10-ml dilution was analyzed, V_{f2B} would be 0.5.

Use Equation 6 to calculate separately the back-half mercury for Fractions 3A, then 3B, then 3C.

$$Hg_{bh3(A,B,C)} = \frac{Q_{bh3(A,B,C)}}{V_{f3(A,B,C)}} \times V_{soln,3(A,B,C)} \quad \text{Eq. 6}$$

where:

- $Hg_{bh3(A,B,C)}$ = total mass of mercury collected separately in Fraction 3A, 3B, or 3C, μg .
- $Q_{bh3(A,B,C)}$ = quantity of mercury in separately analyzed samples, μg .
- $V_{f3(A,B,C)}$ = volume of Fraction 3A, 3B, or 3C analyzed, ml (see Note in Sections 3.1.8.5.1 and 3.1.8.5.2, and calculate similarly).
- $V_{soln,3(A,B,C)}$ = total volume of Fraction 3A, 3B, or 3C, ml.

$$Hg_{bh} = Hg_{bh2} + Hg_{bh3A} + Hg_{bh3B} + Hg_{bh3C} \quad \text{Eq. 7}$$

where:

Hg_{bh} = total mass of mercury collected in the back half of the sampling train, μg .

3.1.8.5.3 Total Train Mercury Catch. Calculate the total amount of mercury collected in the sampling train using Equation 8.

$$Hg_t = (Hg_m - Hg_{mb}) + (Hg_{bh} - Hg_{bb}) \quad \text{Eq. 8}$$

where:

Hg_t = total mass of mercury collected in the sampling train, μg .

Hg_{mb} = blank correction value for mass of mercury detected in front-half field reagent blank, μg .

Hg_{bb} = blank correction value for mass of mercury detected in back-half field reagent blanks, μg .

Note: If the total of the measured blank values ($Hg_{mb} + Hg_{bb}$) is in the range of 0 to 6 μg , then the total may be used to correct the emission sample value ($Hg_m + Hg_{bh}$); if it exceeds 6 μg , the greater of the following two values may be used; 6 μg or 5 percent of the emission sample value ($Hg_m + Hg_{bh}$).

3.1.8.6 Metal Concentration of Stack Gas. Calculate each metal separately for the cadmium, total chromium, arsenic, nickel, manganese, beryllium, copper, lead, phosphorus, thallium, silver, barium, zinc, selenium, antimony, and mercury concentrations in the stack gas (dry basis, adjusted to standard conditions) as follows:

$$C_s = K_4 (M_t / V_{m(std)}) \quad \text{Eq. 9}$$

where:

C_s = concentration of each metal in the stack gas, mg/dscm.

K_4 = 10^{-3} mg/ μg .

M_t = total mass of each metal collected in the sampling train, μg ; (substitute Hg_t for M_t for the mercury calculation).

$V_{m(std)}$ = volume of gas sample as measured by the dry gas meter, corrected to dry standard conditions, dscm.

3.1.8.7 Isokinetic Variation and Acceptable Results. Same as Method 5, Sections 6.11 and 6.12, respectively.

3.1.9 Bibliography

3.1.9.1 Method 303F in Standard Methods for the Examination of Water and Wastewater, 15th Edition, 1980. Available from the American Public Health Association, 1015 18th Street, N.W., Washington, D.C. 20036.

3.1.9.2... EPA Methods 6010, 7000, 7041, 7060, 7131, 7421, 7470, 7740, and 7841, Test Methods for Evaluating Solid Waste: Physical/Chemical Methods. SW-846, Third Edition. September 1988. Office of Solid Waste and Emergency Response, U.S. Environmental Protection Agency, Washington, D.C. 20460.

3.1.9.3 EPA Method 200.7, Code of Federal Regulations, Title 40, Part 136, Appendix C. July 1, 1987.

3.1.9.4 EPA Methods 1 through 5, and 12 Code of Federal Regulations, Title 40, Part 60, Appendix A, July 1, 1987.

APPENDIX E

EXTRACTION/ANALYTICAL METHODS

- Nitroaromatics and Nitramines by HPLC (SP No. 21-16- 8330.1)
- TCLP: Non-volatile (SP No. 21-15-1311.1)
- Metals Digestion: Aqueous Samples by ICP/AA Flame
(OP No. OP-21-15-3020.1)
- Metals Digestion: Soil Samples (SP No. 21-15-3050.1)
- Metals by ICP (OP No. OP 21-15-0200.7)
- Metals Preparation: Mercury Digestion (OP No. 21-15-0245.6)
- Metals: Mercury (SP No. 21-15 0245.1)
- Heat of Combustion by Bomb Calorimeter (Btu), ASTM D240
(SOP No. 15-009)
- Sulfur Content, ASTM D129
- Percent Moisture, Percent Ash, EPA Method 209F
(OP No. 21-15-0160.6)
- Metals Emissions in Exhaust Gases, EPA/530-SW-91-010

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(SP. No. 21-16-8330.1)

Amendments to SOP of Method 8330 (SOP #21-16-8330.1)

1. The SOP for Method 8330 will be followed for analyzing wipe samples and soil, sediment, and water samples. The sample collection and preparation protocol has been added to the Method 8330 SOP and is as follows:
 - Samples will be collected with a glass fiber filter paper saturated with acetonitrile and placed into a 40-mL VOA vial.
 - Samples will be prepared by adding 20 mL of acetonitrile (sufficient volume to cover the filter) into the VOA vial.
 - The samples will be extracted using a 4-hour sonication extraction procedure.
 - The extract will be filtered through a 0.2 micron teflon filter.
 - The filtered extract will be analyzed using the procedure presented in the Method 8330 SOP for soil extracts.
 - Quantification limits for wipe samples have been added to the SOP.
2. The calibration control limits will be $\pm 20\%$ for this project.
3. The following disposal procedures are implemented for the handling and disposal of TNT solutions resulting from explosives analysis:
 - 55-gallon drum - for staging explosives-contaminated soils (i.e., gloves, soils) for future disposal.
 - Paint can - for staging the extracts (vials of liquids) from explosives analysis. The paint cans are lab-packed for shipment and disposal off-site at a permitted facility.
 - 55-gallon drum - for liquids resulting from explosives analysis for shipment and disposal off-site at a permitted facility.
4. The SOP will be used for the analysis of the following compounds: HMX; RDX; 1,3,5-TNB; 1,3-DNB; Tetryl; NB; 2,4,6-TNT; 2,6-DNT; 2,4-DNT; and 2-A-4,6-DNT.
5. Option 2 of the confirmation procedure will be the initial choice, as this option allows for clear data (no-coelutions) for RDX and HMX.



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Historical File: Revision 00: 02/04/91

Reasons for Change:



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1.0

PURPOSE

This method is intended for the analysis of explosives residues in soil, water, or sediment matrices. This method is limited to use by analysts experienced in handling and analyzing explosive residues. Specific compounds are summarized in the following table.

ID	Compound	CAS No.*
HMX	Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine	2691-41-0
RDX	Hexahydro-1,3,5-trinitro-1,3,5-triazine	121-82-4
1,3,5-TNB	1,3,5-Trinitrobenzene	99-35-4
1,3-DNB	1,3-Dinitrobenzene	99-65-0
Tetryl	Methyl-2,4,6-trinitrophenylnitramine	479-45-8
NB	Nitrobenzene	98-95-3
2,4,6-TNT	2,4,6-Trinitrotoluene	118-96-7
2,6-DNT	2,6-Dinitrotoluene	606-20-2
2,4-DNT	2,4-Dinitrotoluene	121-14-2
2-A-4,6-DNT	2-Amino-4,6-dinitrotoluene	355-72-78-2
4-A-2,6-DNT	4-Amino-2,6-dinitrotoluene	1946-51-0
2-NT	2-Nitrotoluene	88-72-2
4-NT	4-Nitrotoluene	99-99-0
3-NT	3-Nitrotoluene	99-08-1

* Chemical Abstracts Service Registry Number



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2.0 REFERENCES

- 2.1 Draft Method 8330, Nitroaromatics and Nitramines by High Performance Liquid Chromatography (HPLC), Revision 0, November 1990. This method was obtained from the US Army Corps of Engineers (COE), as a draft document developed by the COE for submittal and eventual approval for publication in EPA SW846, Test Methods for Evaluating Solid Waste, 3rd Edition.
- 2.2 Supplemental bibliography is given in Section 11.

3.0 SCOPE AND APPLICATION

- 3.1 This method is used to determine the concentration of the compounds listed in Section 1 in a water, soil, or sediment matrix.
- 3.2 This method provides a salting-out extraction procedure for low concentration, i.e., parts per billion (micrograms per liter) of explosives residues in surface or ground water. Direct injection of diluted and filtered water samples can be used for water samples of higher concentration (see Table 1).
- 3.3 All of these compounds are either used in the manufacture of explosives or are the degradation products of compounds used for that purpose. When making stock solutions for calibration, treat each compound as if it were extremely explosive.
- 3.4 The practical quantitation limits (PQL's) of target analytes determined by this method in water and soil are presented in Table 1.
- 3.5 This method is restricted to use by or under the supervision of analysts experienced in the use of HPLC, skilled in the interpretation of chromatograms, and experienced in handling explosive materials.

4.0 SUMMARY OF METHOD

- 4.1 This method provides high performance liquid chromatographic (HPLC) conditions for the detection of ppb levels of certain explosives residues in water, soil and sediment matrix. Prior to use of this method, appropriate sample preparation techniques must be used.



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- 4.2 Low-Level Salting-out Method: Aqueous samples of low concentration are concentrated by a salting-out extraction procedure with acetonitrile and sodium chloride. The acetonitrile extract is further concentrated to less than 1.0 mL using a Kuderna-Danish evaporator and brought to 1.0 mL using acetonitrile. On the day of analysis, dilute 200 μ L extract with 600 μ L of 1:2 methanol/water.
- 4.3 High-Level Direct Injection Method: Aqueous samples of higher concentration can be diluted 1/1 (v/v) with methanol or acetonitrile, filtered, separated on a C-18 reverse phase column, measured at 250 nm, and confirmed on a C-8 reverse phase column.
- 4.4 Soil and sediment samples are extracted using acetonitrile in an ultrasonic bath, filtered and chromatographed as described in Section 9.3.
- 5.0 INTERFERENCES
- 5.1 Solvent reagents, glassware and other sample processing hardware may yield discrete artifacts and/or elevated baselines, causing misinterpretation of the chromatograms. All of these materials must be demonstrated to be free from interferences, under the conditions of the analysis, by running method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required.
- 5.2 2,4-DNT and 2,6-DNT elute at similar retention times on the ODS column. A large concentration of one isomer may mask the response of the other isomer. In this case, it may be possible to quantify both isomers through the use of a second column.
- 5.3 Tetryl decomposes rapidly in methanol/water solutions, as well as with heat. When performing analysis by direct injection, all aqueous samples expected to contain tetryl should be diluted with acetonitrile prior to filtration. All samples expected to contain tetryl should not be exposed to temperatures above room temperature.
- 5.4 Degradation products of tetryl appear as a shoulder on the TNT peak. Peak heights rather than peak areas should be used when tetryl is present in concentrations that are



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significant relative to the concentration of TNT.

6.0 APPARATUS AND MATERIALS

6.1 HPLC System

6.1.1 HPLC: equipped with a pump capable of achieving 4000 psi, a 50- μ L loop injector and a 250-nm UV detector (Perkin Elmer Series 3 or equivalent).

6.1.2 HPLC Columns:

C-18 reverse phase, 25 cm x 4.6 mm (5 μ m particle size):
Dupont Zorbax ODS or equivalent.

C-8 reverse phase, 25 cm x 4.6 mm (5 μ m particle size):
Dupont Zorbax C-8 or equivalent.

6.1.3 Strip Chart Recorder.

6.1.4 Digital Integrator (optional).

6.1.5 Autosampler (optional).

6.2 Other Equipment

6.2.1 Temperature Controlled Ultrasonic Bath.

6.2.2 Vortex Mixer.

6.2.3 Balance, \pm 0.1 mg.

6.3 Materials

6.3.1 High Pressure Injection Syringe: 500 μ L, (Hamilton liquid syringe or equivalent).

6.3.2 Disposable Cartridge Filters: 0.45 μ m Teflon® filter.
0.20 μ m Teflon® filter

6.3.3 Pipettes: 10 mL, 9 mL, 5 mL, 1 mL volumetric, Class A, glass.

6.3.4 Pasteur Pipettes.

6.3.5 Scintillation Vials: 20 mL, glass



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- 6.3.6 Vials: 15 mL glass, Teflon®-lined cap,
 40 mL glass, Teflon®-lined cap,
 4 mL amber glass,
 1.8 mL autosampler.
- 6.3.7 Syringes: 10 µL, 50 µL, 100 µL glass with metal plunger.
 1.0 mL glass with Teflon® plunger.
- 6.3.8 Disposable Syringes: Glaspak, 2.5 mL and 10 mL or
 equivalent.
- 6.3.9 Separatory Funnel: 500 mL.
- 6.3.10 Vacuum Desiccator: glass.
- 6.3.11 Boiling Chips: solvent extracted, approximately 10/40
 mesh (Teflon® or equivalent).
- 6.3.12 Oven: forced air, without heating.

7.0 REAGENTS

- 7.1 HPLC grade chemicals shall be used in all tests. It is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lowering the accuracy of the determination.
- 7.2 Analytical Standards. Standards marked with an asterisk (*) are explosives, requiring special handling. Allow ample lead time (e.g., up to six months) for obtaining these compounds. The primary source for these explosives is through military contracts. Other nitro-compounds are metabolites of the explosives and should be commercially available. However, no easily obtainable source for the amino-DNT's has been found.
- 7.2.1 * HMX: Standard Analytical Reference Material
- 7.2.2 * RDX: Standard Analytical Reference Material
- 7.2.3 NB: Standard Analytical Reference Material.
- 7.2.4 * Tetryl: Standard Analytical Reference Material



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- 7.2.5 * 2,4,6-TNT: Standard Analytical Reference Material
- 7.2.6 2-Amino-2,6-DNT: Reagent grade.
- 7.2.7 4-Amino-2,6-DNT: Reagent grade.
- 7.2.8 2,4-DNT: Standard Analytical Reference Material.
- 7.2.9 2,6-DNT: Standard Analytical Reference Material.
- 7.2.10 1,3,5-TNB: Standard Analytical Reference Material.
- 7.2.11 1,3-DNB: Standard Analytical Reference Material.
- 7.2.12 2-NT: Reagent grade.
- 7.2.13 3-NT: Reagent grade.
- 7.2.14 4-NT: Reagent grade.

7.3 Other Reagents

- 7.3.1 Reagent Water: All references to water in this method refer to water in which an interference is not observed at the detection limit of the compounds of interest. Reagent water can be generated by passing tap water through a carbon filter feed containing about 1 pound of activated carbon. A water purification system may be used to generate organic-free deionized water.
- 7.3.2 Acetonitrile: HPLC grade.
- 7.3.3 Methanol: HPLC grade, distilled in glass.
- 7.3.4 Sodium Chloride, NaCl: Reagent grade. If possible use NaCl from glass bottles. High background levels have been observed from NaCl shipped in plastic containers.
- 7.3.5 Mobile Phase 1: 50% water/34% MeOH/16% ACN
Mobile Phase 2: 60% water/40% ACN
Mobile Phase 3: 60% water/15% MeOH/25% ACN

7.4 Stock Standard Solutions

- 7.4.1 Prepare a separate 10,000 µg/mL stock standard solution for each nitro-compound in the following manner. Dry each analyte standard to constant weight. Accurately



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weigh approximately 50 mg (weigh to 0.1 mg) of a single analyte and dissolve with 5 mL of acetonitrile, measured with a Class A pipet. Store in a refrigerator at 4°C in the dark. Calculate the concentration of the stock solution from the actual weight used. Check stock solutions for stability. Solutions should be stable for at least a year.

7.4 Intermediate Standard Solutions

The target nitro-compound list in the table in Section 1 has been divided into two calibration mixes due to demand (only the first nine listed nitroaromatic compounds are requested for most work plans), potential co-elution problems, and compound availability. For this reason, the Intermediate Standard Solutions A/B represent a composite including only the first nine compounds. Intermediate Standard Solutions C/D comprise the remaining compounds, if the full list is requested.

7.4.1 Intermediate Standard Solutions A and B.

7.4.1.1 Using microliter syringes and volumetric pipettes, prepare composite Standard A as shown in the ensuing table (Table 3 at the end of this method shows actual WESTON measurements), with a final volume of 10 mL in acetonitrile. Using volumetric pipettes prepare a 1:10 dilution of Standard A in acetonitrile, with a 10 mL final volume. This is Standard B. Seal solutions with a Teflon®-lined cap. Store in the dark at 4°C.

INTERMEDIATE CALIBRATION STANDARDS A AND B			
Compound	μL Stock Standard per 10 mL	Standard A Concentration ($\mu\text{g/mL}$) [*]	Standard B Concentration ($\mu\text{g/mL}$) [*]
HMX	100	100	10
RDX	100	100	10
1,3,5-TNB	200	200	20
1,3-DNB	50	50	5
Tetryl	500	500	50
NB	50	50	5
2,4,6-TNT	200	200	20
2,6-DNT	50	50	5
2,4-DNT	50	50	5

^{*} Based on nominal 10 mg/mL Stock Standard, actual volumes and concentrations will vary based on the stock solutions prepared in Section 7.3.1.



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- 7.4.2 Using microliter syringes and volumetric pipettes prepare Standard C as shown below, with a final volume of 10 mL in acetonitrile. Using volumetric pipettes prepare a 1:10 dilution of Standard C in acetonitrile, with a 10 mL final volume. This is Standard D. Seal solutions with a Teflon®-lined cap. Store in the dark at 4°C.

INTERMEDIATE CALIBRATION STANDARDS C AND D			
Compound	μ L Stock Standard per 10 mL	Standard C Concentration (μ g/mL)*	Standard D Concentration (μ g/mL)*
2-Amino-4,6-DNT	100	100	10.0
4-Amino-2,6-DNT	100	100	10.0
2-Nitrotoluene	100	100	10.0
3-Nitrotoluene	100	100	10.0
4-Nitrotoluene	100	100	10.0
* Based on nominal 10 mg/mL Stock Standard, actual volumes and concentration will vary based on the stock solutions prepared in Section 7.3.1.			

7.5 Working Standards

On the day of analysis, prepare a series of nine calibration standards and a calibration blank with relative concentrations of 0.5X to 200X (instructions follow), where X is close to the PQL (see Table 1). Note, for the low-level method: 0.1 μ g/mL calibration X 10 = 1 μ g/L sample.

Based on nominal 10 mg/mL Stock Standard, actual concentration will vary based on the stock solutions prepared in Section 7.3.1 and Intermediate Standards prepared in Section 7.4.

In most cases, the requested compound list only includes the nine compounds from Standard A/B, in which case preparation of Standard C/D would not be required.

Using the ensuing table as reference in this section (see Table 4 at the end of this method for actual amounts used by WESTON), place the indicated amounts of mobile phase into 1.8 mL autosampler vials. Inject the indicated amounts of Standards A and B or Standards C and D into the mobile phase with a microliter syringe. Seal the vial with a Teflon®-lined or Viton® septum and cap. Mix well. Prepare fresh daily and keep in the dark until used.



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TABLE 4. WORKING CALIBRATION STANDARDS

Rel. Conc. -		Concentration ($\mu\text{g/mL}$) [*]								
		0.5X	1.0X	2.0X	4.0X	10X	20X	40X	100X	200X
Intermed Calib Std (μL)	A/C -	0.0	0.0	0.0	0.0	0.0	12.5	25.0	62.5	125
	B/D -	3.12	6.25	12.5	25.0	62.5	0.0	0.0	0.0	0.0
μL Mobile Phase I -		997	994	988	975	938	988	975	938	875
HMX		0.0312	0.0625	0.125	0.250	0.625	1.25	2.50	6.25	12.5
RDX		0.0312	0.0625	0.125	0.250	0.625	1.25	2.50	6.25	12.5
1,3,5-TNB		0.0625	0.125	0.250	0.500	1.25	2.50	5.00	12.5	25.0
1,3-DNB		0.0156	0.0312	0.0625	0.125	0.312	0.625	1.25	3.12	6.25
NB		0.0156	0.0312	0.0625	0.125	0.312	0.625	1.25	3.12	6.25
Tetryl		0.156	0.312	0.625	1.25	3.125	6.25	12.5	31.2	62.5
2,4,6-TNT		0.0625	0.125	0.250	0.500	1.25	2.50	5.00	12.5	25.0
2,6-DNT		0.0156	0.0312	0.0625	0.125	0.312	0.625	1.25	3.12	6.25
2,4-DNT		0.0156	0.0312	0.0625	0.125	0.312	0.625	1.25	3.12	6.25
2-A-4,6-DNT		0.0312	0.0625	0.125	0.250	0.625	1.25	2.50	6.25	12.5
4-A-2,6-DNT		0.0312	0.0625	0.125	0.250	0.625	1.25	2.50	6.25	12.5
2-NT		0.0312	0.0625	0.125	0.250	0.625	1.25	2.50	6.25	12.5
4-NT		0.0312	0.0625	0.125	0.250	0.625	1.25	2.50	6.25	12.5
3-NT		0.0312	0.0625	0.125	0.250	0.625	1.25	2.50	6.25	12.5

7.6 Surrogate Standards

7.6.1 The analyst should monitor the performance of the extraction and analytical system and the effectiveness of the method in dealing with each sample matrix by spiking each sample, matrix spike, and reagent water blank with one or two surrogates (e.g., 3-NT or analytes not expected to be present in the sample).

7.7 Prepare HPLC eluent by combining solvent(s) and water on a volume/volume basis in the percentages stated in the Instrument Conditions (Section 9.2)

8.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

8.1 Grab samples must be collected and stored in glass containers. Follow conventional sampling procedures.



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8.2 Samples must be kept below 4°C and in the dark from the time of collection through analysis, except during drying.

8.3 Soil and sediment samples should be air dried to constant weight at room temperature or colder after collection.

8.4 All water samples must be extracted within 7 days of collection and analyzed within 40 days after extraction. All soil and sediment samples must be extracted within 14 days of collection and analyzed within 40 days after extraction.

9.0 PROCEDURE

9.1 Sample Preparation: Aqueous Samples

Option 1: The low-level method may be used for all samples, provided they are diluted into the calibration range when necessary.

Option 2: If both low-level and high level methods are to be used, it is highly recommended that all samples of this type be screened with the high-level method (>50 µg/L) to determine if the low-level method (1-50 µg/L) is required.

9.1.1 Low-Level Method (Salting-Out Extraction)

9.1.1.1 Place a 400 mL aliquot of water sample in a 500 mL separatory funnel and add 130 g of NaCl. Vigorously shake the sample until all of the NaCl is completely dissolved. Be sure to dissolve all salt before adding acetonitrile, or the dissolution process takes much longer.

9.1.1.2 Add a 100 mL volume of acetonitrile using a glass volumetric pipette. Shake the separatory funnel vigorously for 5 minutes. Allow the funnel to stand undisturbed for 30 minutes while the two phases separate. Discard the water (lower) layer and collect the acetonitrile (upper) layer (approximately 23 mL) in a 40 mL Teflon®-capped vial. Rinse the separatory funnel with 5 mL of acetonitrile and add the rinsate to the extract.

9.1.1.3 If the collected extract was turbid, centrifuge the 40 mL



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vial at 4000 rpm's for 5 minutes. Remove the acetonitrile (upper) layer with a Pasteur pipette and transfer it to a clean vial.

9.1.1.4 Concentrate sample to approximately 1 mL using a gentle stream of nitrogen. Transfer quantitatively to a 4 mL amber vial, pre-marked at the 1.0 mL line. Concentrate the sample to 1.0 mL.

9.1.1.5 On the day of analysis, dilute 200 μ L of extract with 600 μ L of 2:1 water/methanol.

9.1.2 High-Level Method

9.1.2.1 Sample filtration: Place a 5 mL aliquot of each water sample in a scintillation vial, add 5 mL of acetonitrile, shake thoroughly, and filter through a 0.45 μ m Teflon® filter. Discard the first 3 mL of filtrate, and retain the remainder in a Teflon®-capped vial for RP-HPLC analysis as in Section 9.5. HMX quantitation can be improved with the use of methanol rather than acetonitrile for dilution before filtration. However, according to Section 5.3, the use of methanol may affect tetraol stability.

9.2 Sample Preparation: Soil and Sediment Samples

9.2.1 Sample homogenization: Dry soil samples in air at room temperature or colder, being careful not to expose the sample to direct sunlight. Pulverize the sample with a spatula and remove any sticks, rocks or otherwise extraneous material. Particle size should resemble soil passed through a 30 mesh sieve.

Note: See safety section regarding extraction of wet soils for high level samples.

9.2.2 Sample extraction

9.2.2.1 Place a 2.0 g subsample of each soil sample in a 15 mL glass vial. Add 10.0 mL of acetonitrile, cap with a Teflon®-lined cap, and place in an cooled ultrasonic bath for 18 hours.

9.2.2.2 After sonication, allow the sample to settle for 30 minutes.



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9.2.2.3 Place supernatant in a disposable syringe and filter through a 0.2 micron Teflon® filter.

9.2.2.4 On day of analysis, dilute 200 µL of sample with 600 µL of 2:1 water/methanol.

9.3 Chromatographic Conditions

Primary Column:	DuPont Zorbax ODS, or equivalent (C-18 Reverse Phase HPLC Column, 250 mm X 4.6 mm ID, 5 micron particle size)
Mobile Phase:	50% water/34% MeOH/16% ACN
Flow Rate:	1.5 mL/min
Injection volume:	50 µL
UV Detector:	250 nm
Secondary Column: (Option 1)	Dupont Zorbax C-8, or equivalent (C-8 Reverse Phase HPLC Column, 250 mm x 4.6 mm ID, 5 micron particle size)
Mobile Phase:	60% water/40% ACN
Flow Rate:	1.5 mL/min
Injection Volume:	50 µL
UV Detector:	250 nm
Secondary Column: (Option 2)	Dupont Zorbax C-8, or equivalent (C-8 Reverse Phase HPLC Column, 250 mm x 4.6 mm ID, 5 micron particle size)
Mobile Phase:	60% water/15%MeOH/25% ACN
Flow Rate:	1.5 mL/min
Injection Volume:	50 µL
UV Detector:	250 nm

9.4 Calibration of HPLC

9.4.1 All electronic equipment is allowed to warm up for thirty minutes. During this period, at least 15 void volumes of mobile phase are passed through the column (approximately 20 min at 1.5 mL/min) and continued until the baseline is level at the UV detector's greatest sensitivity.



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9.4.2 Analyze the working standards using the chromatographic conditions given in Section 9.3. Prepare a calibration curve using peak heights or peak areas, as appropriate. The calibration curve should be linear with a zero intercept. Analyze a series of calibration standards for each 24 hour period of analysis.

9.4.3 Analyze a midpoint standard after every ten injections and at the end of the analysis scheme. The response should agree within $\pm 25\%$ of the initial response, or all samples analyzed after the last acceptable calibration will be reanalyzed with a new calibration curve.

9.5 HPLC Analysis

9.5.1 Analyze the samples using the chromatographic conditions given in Section 9.3. All positive measurements observed on the C-18 column must be confirmed by injection onto the C-8 column.

9.5.2 In limited applications (e.g., aqueous process wastes), direct injection of filtered and diluted sample into the HPLC system with a 50 μL loop may be appropriate. The quantitation limits are high, therefore, it is only permitted where concentrations in excess of 50 $\mu\text{g/L}$ are expected.

9.5.3 Dilute samples as necessary to obtain results within the calibration range for each analyte. Calculate the RT window daily using all standards analyzed. Positive results are within 3 standard deviations of the mean retention time for each component. ---

9.5.4 Table 2 summarizes the estimated retention times on both C-18 and C-8 columns for a number of analytes analyzable using this method.

9.5.5 Record the resulting peak sizes in peak heights or area units. The use of peak heights is recommended to improve reproducibility of low level samples.

9.5.6 Initial calibration data are entered into a calculator or computer program for least squares regression using the responses as Y values and target concentrations as X values. The program will calculate an equation to describe the data. The general form of the equation is:



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$Y = aX + b$, $Y = \text{response}$
 $X = \text{true concentration}$
 $a = \text{slope of the regression line}$
 $b = Y \text{ intercept } (X = 0)$

Concentrations of samples are derived from the least squares regression of the initial calibration data. Values of a and b are obtained from the computer regression calculations.

- 9.5.7 Calculate results in the original matrix, using the following information:

$\mu\text{g/mL}$ = concentration of the sample from the daily least squares fit.

DF = dilution required. All preparation schemes in this method have one dilution, prior to instrument analysis.

L or g = liters or grams, i.e., sample size

Calculate the final result using the following equations:

- Low-Level Water: $\mu\text{g/mL} \times \text{DF} \div 0.4 \text{ L} = \mu\text{g/L}$
- High-Level Water: $\mu\text{g/mL} \times \text{DF} \times 1,000 = \mu\text{g/L}$
- Soil: $\mu\text{g/mL} \times 10 \times \text{DF} \div \text{g} = \mu\text{g/g}$

- 9.5.8 If analytical interferences are suspected, or for the purpose of confirmation, analysis using the second HPLC column is required.

10.0 QUALITY CONTROL

- 10.1 Prior to preparation of stock solutions, acetonitrile, methanol, and water blanks should be run to determine possible interferences with analyte peaks. If the acetonitrile, methanol, or water blanks show contamination, a different batch should be used.

- 10.2 Each analytical batch comprises up to 20 samples. For each batch, the following minimum QC should be performed:

Method Blank
Matrix Spike
Matrix Spike Duplicate or Sample Duplicate



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Spike samples at ten times the detection limit. Perform spikes with standards prepared independently from the calibration mix. Recoveries must be within laboratory quality control limits. Investigate any out of control analytes. Identify the cause of the non-conformance, take corrective action to fix the problem, verify that the system is returned to control, and document all actions proposed and taken. Forward a copy of the corrective action documentation to the QA Section. Reanalyze any negatively impacted samples.

10.3 Method Blanks

10.3.1 Method blanks for the analysis of aqueous samples should be reagent water carried through all sample storage, preparation and handling procedures.

10.3.2 Method blanks for the analysis of soil samples should be uncontaminated soil carried through all sample storage, extraction and handling procedures.

11.0 SUPPLEMENTAL REFERENCES

11.1 Bauer, C.F., T.F. Jenkins, S.M. Koza, P.W. Schumacher, P.H. Miyares and M.E. Walsh (1989). Development of an analytical method for the determination of explosive residues in soil. Part 3. Collaborative test results and final performance evaluation. USA Cold Regions Research and Engineering Laboratory, CRREL Report 89-9.

11.2 Grant, C.L. A.D. Hewitt and T.F. Jenkins (1989) Comparison of low concentration measurement capability estimates in trace analysis: Method Detection Limits and Certified Reporting Limits. USA Cold Regions Research and Engineering Laboratory, Special Report 89-20.

11.3 Jenkins, T.F., C.F. Bauer, D.C. Leggett and C.L. Grant (1984) Reversed-phase HPLC method for analysis of TNT, RDX, HMX and 2,4-DNT in munitions wastewater. USA Cold Regions Research and Engineering Laboratory, CRREL Report 84-29.

11.4 Jenkins, T.F. and M.E. Walsh (1987) Development of an analytical method for explosive residues in soil. USA Cold Regions Research and Engineering Laboratory. CRREL Report 87-7.



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- 11.5 Jenkins, T.F., P.H. Miyares and M.E. Walsh (1988a) An improved RP-HPLC method for determining nitroaromatics and nitramines in water. USA Cold Regions Research and Engineering Laboratory, Special Report 88-23.
- 11.6 Jenkins, T.F., P.W. Schumacher, M.E. Walsh and C.F. Bauer (1988b) Development of an analytical method for the determination of explosive residues in soil. Part II: Further development and ruggedness testing. USA Cold Regions Research and Engineering Laboratory. CRREL Report 88-8.
- 11.7 Leggett, D.C., T.F. Jenkins and P.H. Miyares (1990) Salting-out solvent extraction for pre-concentration of neutral polar organic solutes from water. Analytical Chemistry, 62: 1355-1356.
- 11.8 Miyares, P.H. and T.F. Jenkins (1990) Salting-out solvent extraction for determining low levels of nitroaromatics and nitramines in water. USA Cold Regions Research and Engineering Laboratory, Special Report 90-30.
- 12.0 **SAFETY**
- 12.1 Standard precautionary measures used for handling other organic compounds should be sufficient for safe handling of the analytes targeted by this method.
- 12.2 If samples are suspected of containing 10% or greater of explosives, the samples should be extracted without drying and reported on a wet weight basis. The laboratory may institute a screening program for wet soils, at its option.



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TABLE 1. PRACTICAL QUANTITATION LIMITS

COMPOUND	LOW-LEVEL WATER ($\mu\text{g/L}$)	HIGH LEVEL WATER ($\mu\text{g/L}$)	SOIL/SEDIMENT ($\mu\text{g/g}$)
HMX	0.625	125	1.25
RDX	0.625	125	1.25
1,3,5-TNB	1.25	250	2.50
1,3-DNB	0.313	62.5	0.625
Tetryl	3.125	62.5	6.25
NB	0.313	62.5	.625
2,4,6-TNT	1.25	250	2.50
2,6-DNT	0.313	62.5	0.625
2,4-DNT	0.313	62.5	0.625
2-A-4,6-DNT	0.625	125	1.25
4-A-2,6-DNT	0.625	125	1.25
2-NT	0.625	125	1.25
4-NT	0.625	125	1.25
3-NT	0.625	125	1.25

TABLE 2. RETENTION TIME OF ANALYTES BY HPLC
(ANALYZED ACCORDING TO CONDITIONS SPECIFIED IN THIS OP)

COMPOUND	ODS Primary Column (minutes)	C8 Confirmation Column (minutes)	
		Option 1	Option 2
HMX	3.21	7.50*--	8.89
RDX	4.05	7.70*	9.59
1,3,5-TNB	5.96	11.60	- 13.50*
1,3-DNB	6.85	10.63	13.50*
Tetryl	8.01	25.00	28.50
NB	8.47	11.10	14.28
2,4,6-TNT	10.06	19.12	25.75
2,6-DNT	10.68	16.34	24.05
2,4-DNT	10.95	16.15	23.12
2-A-4,6-DNT	9.65*	12.40	19.67
4-A-2,6-DNT	9.65*	12.90	20.86
2-NT			
4-NT			
3-NT			
* Coelute			



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TABLE 3. WESTON VOLUMES/CONCENTRATIONS FOR INTERMEDIATE CALIBRATION STANDARDS A AND B

Compound	μL Stock Standard per 10 mL	Standard A Concentration ($\mu\text{g/mL}$) [*]	Standard B Concentration ($\mu\text{g/mL}$) [*]
HMX	127	127	12.7
RDX	98.0	98.0	9.80
1,3,5-TNB	209	209	20.9
1,3-DNB	59.0	59.0	5.9
Tetryl	41.9	41.9	4.19
NB	500	500	50.0
2,4,6-TNT	192	192	19.2
2,6-DNT	40.0	40.0	4.00
2,4-DNT	42.0	42.0	4.20

^{*} Based on nominal 10 mg/mL Stock Standard, actual volumes will vary based on the stock solutions prepared in Section 7.3.1.

TABLE 4. WESTON VOLUMES/CONCENTRATIONS FOR WORKING CALIBRATION STANDARDS

		Concentration ($\mu\text{g/mL}$) [*]								
Rel. Conc. -		0.5X	1.0X	2.0X	4.0X	10X	20X	40X	100X	200X
Intermed Calib Std (μL)	A/C [*] -	0.0	0.0	0.0	0.0	0.0	12.5	25.0	62.5	125
	B/D [*] -	3.12	6.25	12.5	25.0	62.5	0.0	0.0	0.0	0.0
μL Mobile Phase I -		997	994	988	975	938	988	975	938	875
HMX		0.0397	0.0794	0.159	0.317	0.794	1.59	3.17	7.94	15.9
RDX		0.0306	0.0612	0.123	0.245	0.612	1.23	2.45	6.12	12.3
1,3,5-TNB		0.0655	0.131	0.261	0.522	1.31	2.61	5.22	13.1	26.1
1,3-DNB		0.0184	0.0368	0.0737	0.147	0.368	0.737	1.47	3.68	7.37
NB		0.0131	0.0262	0.0524	0.105	0.262	0.524	1.05	2.62	5.24
Tetryl		0.156	0.312	0.625	1.25	3.125	6.25	12.5	31.2	62.5
2,4,6-TNT		0.0600	0.120	0.240	0.480	1.20	2.40	4.80	12.0	24.0
2,6-DNT		0.0125	0.0250	0.500	0.100	0.250	0.500	1.00	2.50	5.00
2,4-DNT		0.0131	0.0262	0.0525	0.105	0.262	0.525	1.05	2.62	5.25
2-A-4,6-DNT		0.0312	0.0625	0.125	0.250	0.625	1.25	2.50	6.25	12.5
4-A-2,6-DNT		0.0312	0.0625	0.125	0.250	0.625	1.25	2.50	6.25	12.5
2-NT		0.0312	0.0625	0.125	0.250	0.625	1.25	2.50	6.25	12.5
4-NT		0.0312	0.0625	0.125	0.250	0.625	1.25	2.50	6.25	12.5
3-NT		0.0312	0.0625	0.125	0.250	0.625	1.25	2.50	6.25	12.5

^{*} In most cases, the requested compound list only includes the nine compounds from Standard A/B, in which case preparation of Standard C/D would not be required.

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TABLE 5. HPLC ANALYSIS LOG

[illegible]

TCLP: NON-VOLATILE (SP NO. 21-15-1311.1)

Amendments to Method 1311 (OP #21-15-1311.1)

1. Only TCLP metals will be leached and analyzed.
2. A copy of the TCLP preparation sheet will be provided as part of the deliverable data.
3. In addition to method blanks, TCLP extraction blanks will be analyzed at a frequency of 10% of the analytical batch.
4. Control limits for MS recoveries will be +/- 50%. Spikes will consist of target compounds at or below the appropriate regulatory levels.



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INORGANIC ANALYSIS PROTOCOLS
TOXICITY CHARACTERISTIC LEACHING PROCEDURE (TCLP)
INORGANICS AND ORGANICS (Non-Volatile)

These Approval Signatures Are Kept on File
with WESTON's Analytics Division
QA Standard Practice Records

REVISION NUMBER: 04

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Historical File:

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Revision 01:	11/01/88	OP 21-15-1310.1
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Revision 04:	03/15/91	

Reasons for Change, Revision 04:

- edited to reflect regulation changes in 40 CFR 261
- format changes



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INORGANIC ANALYSIS PROTOCOLS
TOXICITY CHARACTERISTIC LEACHING PROCEDURE (TCLP)
INORGANICS AND ORGANICS (Non-Volatile)

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REVISION NUMBER: 04

1.0 **PURPOSE**

Preparation of an extract (leachate) from a liquid, solid, or multiphasic waste which is then analyzed to determine toxicity based on the mobility of the organic and inorganic analytes present. This operating practice (OP) specifically addresses non-volatile contaminants. Volatile contaminants are addressed in WESTON OP 21-15-1311.2.

2.0 **REFERENCES**

Federal Register 40 CFR, Part 268, Appendix I - Toxicity Characteristic Leaching Procedure, 7 November 1986. (Note: this reference in its entirety is updated in the ensuing 40 CFR 261 references)

Federal Register 40 CFR, Part 261, Appendix II - Toxicity Characteristic Leaching Procedure, 13 November 1986. (Note: this reference in its entirety is updated in the ensuing 40 CFR 261 references)

Federal Register 40 CFR, Part 261, 29 March 1990. (Note: parts of this reference, including Appendix II in its entirety, are updated in the ensuing 29 June 1990 reference)

Federal Register 40 CFR, Part 261, Appendix II - Method 1311, Toxicity Characteristic Leaching Procedure, 29 June 1990



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3.0 PRINCIPLE/DISCUSSION

The Toxicity Characteristic Leaching Procedure (TCLP) is designed to determine the mobility of both organic and inorganic contaminants present in liquid, solid and multi-phasic wastes. A representative sample is extracted with a buffered solution to simulate the leaching of hazardous contaminants that may occur when a waste is co-disposed with municipal wastes in a sanitary landfill.

Two distinct methods are utilized depending on whether volatile organics (VOA's) or non-volatile constituents (i.e., other organics and metals) are to be analyzed. Volatile constituents require a specialized Zero Headspace Extractor (ZHE) apparatus for volatile sample preparation (WESTON OP 21-15-1311.2).

For solid wastes or wastes that contain significant amounts of solid material, the particle size is reduced and the liquid phase (if any) is separated from the solid phase and stored for later analysis. The solid phase is extracted with an amount of extraction fluid that is equal to 20 times the weight of the solid material.

For VOA's, the liquid and solid phases are separated by filtering prior to and after the extraction. For all other parameters, the liquid and solid phases are separated after the extraction.

The extract (leachate) is analyzed according to the requirements of the regulatory program dictating the TCLP, to determine one or more of the following:

- (1) is the waste hazardous and therefore subject to regulation under Subtitle C of the Resource Conservation and Recovery Act (RCRA),
- (2) does the hazardous waste comply with Land Ban Disposal Restrictions, or
- (3) does solidification treatment of the waste effectively reduce mobility of analytes of concern.

The most common reason for doing TCLP is item (1). The analyte lists and regulatory action limits described in this operating practice are based on this requirement, per 40 CFR 261.

Although specific QC requirements may vary, depending on the EPA Region, minimally a matrix spike will be performed on each waste



type, to allow correction of the measured values for matrix bias. A portion of the extract (leachate) for metallic contaminant determinations is spiked with spiking standards and acidified with nitric acid to a pH < 2.

The sample is then analyzed by the appropriate method for organic and metal constituents.

Refer to Figure 1 for the TCLP Flowchart and Tables 1 and 2 for a listing of the TC constituents and Regulatory Levels.

4.0 INTERFERENCES

Since this is a preparation procedure, interferences will only become apparent at the spiking and analysis stage. Interferences for spiking and the instrumentation are discussed in the spiking and instrument SOPs.

A physical interference may occur for the pH readings if the waste material is high in organic material (such as an oil). The waste may coat the pH probe, which affects the ability to obtain an accurate reading. When this type of interference occurs, pH paper is used instead of a meter for the final pH measurement. The use of pH paper is noted in the laboratory notebook.

5.0 INSTRUMENTATION AND APPARATUS/EQUIPMENT

5.1 Agitation Apparatus: The extractor is a custom made rotary type design that meets the specifications of tumbling the sample extraction vessels end-over-end at a rate of 30 ± 2 rpm.

5.2 Bottle Extraction Vessels:

- 1-liter plastic bottles - when metals only are requested
- 2.5-liter borosilicate glass bottles (plastic coated for safety) - for organics (BNA, Herb/Pest) or organics plus metals

5.3 Filtration Apparatus for % Solids Determination: pressure filter using compressed nitrogen as the purge gas.

5.3 Filter Paper: borosilicate glass fiber, 0.6 - 0.8 um pore size acceptable (0.7 um used at time this OP was



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initiated). Fragile, handle with care.

Filters need to be acid-washed prior to use when evaluating metals: rinse with 1 N HNO_3 followed by three consecutive rinses with deionized water (a minimum of 1 L per rinse is recommended). Acid-washed filters may be used for non-volatile extractions even if metals are not of concern; however, they must be used if metals are of concern.

- 5.4 pH Meter: accurate to ± 0.06 units @ 25°C
- 5.5 Laboratory Balance: capable of reading ± 0.01 g
- 5.6 Beaker or Erlenmeyer Flask: glass, 250 mL
- 5.7 Watchglass or Aluminum Foil: appropriate diameter to cover beaker or Erlenmeyer flask
- 5.8 Agitator Bath, to hold twelve 250 mL beakers
- 5.9 Ruler, Graduated: to aid with particle size reduction
- 6.0 PREVENTIVE MAINTENANCE

The main preventive maintenance required is keeping the area and all equipment clean and free of contaminants.

The pH probe should be checked periodically for bubbles. The probes are replaced when needed.

7.0 REAGENTS

7.1 Hydrochloric Acid (HCl), 1.0 N

83 mL of concentrated hydrochloric acid is carefully added to a 1 L volumetric flask containing approximately 400 mL deionized water. The flask is swirled to mix the hydrochloric acid and water. The solution is brought up to volume and mixed.

Life of Reagent: one year
Storage Requirements: none

7.2 Nitric Acid (HNO_3), 1.0 N

64 mL of concentrated nitric acid is carefully added to



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a 1 L volumetric flask containing approximately 400 mL deionized water. The flask is swirled to mix the acid and water. The solution is brought up to volume and mixed.

Life of Reagent: one year
Storage Requirements: none

7.3 Sodium Hydroxide (NaOH), 1.0 N

40.0 g of sodium hydroxide pellets are added to a 1 L volumetric flask containing approximately 800 mL deionized water. After the pellets are dissolved, the solution is brought up to volume and mixed well. The flask should be placed in a cool water bath when mixing since the reaction produces a great amount of heat.

Life of Reagent: one year
Storage Requirements: none

7.4 Extraction Fluid #1

5.7 mL of glacial acetic acid is added to 500 mL deionized water in a 1 L volumetric flask. 64.3 mL of 1.0 N sodium hydroxide is added and the volume is adjusted to 1 L with DI water. The pH of the solution should be 4.93 +/- 0.05.

Life of Reagent: one day
Storage Requirements: none

7.5 Extraction Fluid #2

5.7 mL of glacial acetic acid is added to 500 mL deionized water in a 1 L volumetric flask. The volume is adjusted to 1 L using deionized water. The pH of the properly prepared solution should be 2.88 +/- 0.05.

Life of Reagent: one day
Storage Requirements: none

8.0 PRELIMINARY EVALUATION: % SOLIDS AND PARTICLE SIZE

This preliminary sample evaluation must be performed for both ZHE and non-volatile TCLP. Information about %solids and particle size reduction obtained from the non-volatile TCLP (OP 21-15-1311.1) can be used for the ZHE (OP 21-15-1311.2). In fact, the section



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"Determination of % Solids" is identical in both methods. However, none of the sub-samples used to make these determinations from the non-volatiles method can be used in Section 9.0 of the ZHE procedure. Fresh aliquots must be used.

Although a minimum sample size of 100 grams is required, a larger sample size may be necessary, depending on the percent solids of the waste sample. Enough waste sample should be collected such that at least 75 grams of the solid phase of the waste (as determined using glass fiber filter filtration) is extracted. This will ensure that there is adequate extract for the required analyses (semivolatiles, metals, pesticides and herbicides).

The determination of which extraction fluid to use (see Section 8.2.12) may also be conducted at the start of this procedure. This determination shall be on the solid phase of the waste (as obtained using glass fiber filter filtration).

8.1 Determination of % Solids

- 8.1.1 If the waste will obviously yield no free liquid (e.g., is 100% solids) when subjected to pressure filtration, proceed to Section 8.2 for particle size evaluation.
- 8.1.2 If the sample is liquid or multi-phasic, liquid/solid separation is required. This involves the filtration procedure outlined in Sections 8.1.2.1 to 8.1.2.7.
 - 8.1.2.1 Pre-weigh the filter and the container which will receive the filtrate.
 - 8.1.2.2 Assemble the filter holder and filter.
 - 8.1.2.3 Weigh out a representative 100 g sub-sample of the waste and record the weight.
 - 8.1.2.4 Allow slurries to stand to permit the solid phase to settle. Wastes that settle slowly may be centrifuged prior to filtration.
 - 8.1.2.5 Quantitatively transfer the waste sample to the filter holder (liquid and solid phase). Spread the waste evenly over the surface of the filter. If filtration of the waste at 4°C reduces the amount of expressed liquid over what would be expressed at room temperature, then allow the sample to warm up to room temperature in the filtering device before filtering.



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Note: If waste material (>1% of the original sample weight) has obviously adhered to the container used to transfer the sample to the filtration apparatus, determine the weight of this residue and subtract it from the sample weight determined in Section 8.1.2.3 to determine the weight of the waste sample which will be filtered.

Gradually apply pressure of 10 psi, until gas moves through the filter. If this point is not reached under 10 psi, and if no additional liquid has passed through the filter in any two minute interval, slowly increase the pressure in 10 psi increments to a maximum of 50 psi. After each incremental increase of 10 psi, if the pressurizing gas has not moved through the filter in any two minute interval, proceed to the next 10 psi increment. When the pressurizing gas begins to move through the filter, or when liquid flow has ceased at 50 psi, filtration is stopped.

- 8.1.2.6 The material in the filter holder is defined as the solid phase of the waste, and the filtrate is defined as the liquid phase.

Note: Some wastes, such as oily wastes and some paint wastes will obviously contain some material that appears to be a liquid. Even after applying pressure filtration this material may not filter. In this case, the material within the filtration device is defined as a solid and is carried through the extraction as a solid. Do not replace the original filter with a fresh filter. Use only one filter.

- 8.1.2.7 Determine the weight of the liquid phase by subtracting the total weight of the filtrate container (see Section 8.1.2.1) from the total weight of the filtrate-filled container. The liquid phase cannot be used for VOA analysis. However, if non-volatile analysis of the TCLP extract is required, the liquid phase may now be either analyzed (see OP 21-15-1311.1) or stored at 4°C until time of analysis. The weight of the solid phase of the waste sample is determined by subtracting the weight of the liquid phase from the weight of the total waste sample, as determined in Section 8.1.2.3 or under "note" in Section 8.1.2.5. Record the weight of the liquid and solid phases. Calculate the percent solids as follows:



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$$\% \text{ Solids} = \frac{\text{Weight of the Solid}}{\text{Total Weight of Waste}} \times 100$$

8.1.2.8 Determine the percent solids on a dry weight basis as follows:

8.1.2.8.1 Remove the solid phase and filter from the filtration apparatus.

8.1.2.8.2 Dry the filter and solid phase at 100°C until two successive weighings yield the same value. Record the final weight.

Safety Note: Caution should be taken to ensure that the subject solid will not flash upon heating. It is recommended that the drying oven be vented to a hood or other appropriate device.

8.1.2.8.3 Calculate the percent dry solids as follows:

$$\% \text{ Dry Solids} = \frac{\text{Weight of Tared Weight Waste and Filters - of Filters}}{\text{Initial Weight of Waste}} \times 100$$

8.1.2.9 If the solid phase is <0.5% dry solids of the waste, particle size evaluation is not required.

8.1.2.10 If the solid phase is ≥0.5% dry solids of the waste, proceed to Section 8.2. Obtain a fresh sample aliquot for particle size determination.

8.2 Determination of Particle Size

8.2.1 Obtain a fresh portion of the waste sample. Using the solid phase of the waste (process it through Sections 8.1.1 through 8.1.2.6 to obtain the solid phase, wet weight), evaluate the sample for particle size. If the solid material is capable of passing through a 9.5 mm sieve (i.e., smaller than 1 cm in its narrowest dimension), the particle size reduction is not required.

8.2.2 If the particle size is larger than 9.5 mm, particle size reduction by crushing, cutting, or grinding is required. Special precautions must be taken in this step for VOA TCLP extractions. Refer to OP 21-15-1311.2.

8.3 Determination of Extraction Fluid to Use



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- 8.3.1 Weigh out a small sub-sample of the solid phase of the waste, reduce the solid (if necessary) to a particle size of approximately 1 mm in diameter or less, and transfer a 5.0 g portion to a 100 mL beaker.
- 8.3.2 Add 96.5 mL DI water, cover with watch glass, and stir vigorously for five minutes using a magnetic stirrer or agitator bath. Measure and record the pH. If the pH is ≤ 5.0 , extraction fluid # 1 is used. Proceed to Section 9.0.
- 8.3.3 If the pH from Section 8.3.2 is >5.0 , add 3.5 mL 1.0 N hydrochloric acid, stir for 30 seconds, cover with a watch glass, and heat to 50°C. Continue heating at 50°C for ten minutes.
- 8.3.4 Let the solution cool to room temperature and record the pH. If pH is ≤ 5.0 , use extraction fluid #1. If the pH is > 5.0 , use extraction fluid #2.

9.0 PROCEDURE FOR NON-VOLATILES

9.1 Sample Size: Inorganics & Semi-Volatiles

Samples containing 100% solids.....100 g solid
Samples containing 0.5% - 99.9% solids.....100 g solid
ideally, 75.0 g solid minimum (dry weight)

9.2 Procedure

- 9.2.1 Transfer the solid material into the extractor vessel, including the filter used to separate the initial liquid from the solid phase.

Note: If any of the solid phase remains adhered to the walls of the filter holder, or the container used to transfer the waste, its weight shall be determined, subtracted from the weight of the solid phase of the waste, as determined above, and this weight is used in calculating the amount of extraction fluid to add into the extractor bottle.

Slowly add an amount of the appropriate extraction fluid into the extractor bottle equal to 20 times the weight of the solid phase that has been placed into the extractor bottle. Close the extractor bottle tightly, and place in the rotary extractor and rotate for 18 ± 2 hours. The



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ambient room temperature shall be maintained at $23 \pm 2^{\circ}\text{C}$ during the extraction period.

9.2.2 Following the 18 hour extraction, the material in the extractor vessel is separated into its component liquid and solid phases by filtering through a new glass fiber filter as outlined in Section 8.1.2.5.

9.3 The TCLP extract is now prepared as follows:

9.3.1 If the waste contained no initial liquid phase, the filtered liquid material obtained from Section 9.2.2 is defined as the TCLP extract. Proceed to Section 9.4.

9.3.2 If compatible (e.g., will not form precipitate or multiple phases), the filtered liquid resulting from Section 9.2.2 is combined with the initial liquid phase of the waste as obtained in Section 8.1.2.7. This combined liquid is defined as the TCLP extract.

9.3.3 If the initial liquid phase of the waste, as obtained from Section 8.1.2.7 is not compatible with the filtered liquid resulting from Section 9.2.2, the liquids are not combined. The liquids are collectively defined as the TCLP extract and are analyzed separately.

9.4 The TCLP extracts are prepared according to the procedures for the particular analysis (organics or metals) before being analyzed.

10.0 CALCULATIONS AND REPORTING RESULTS

All data is recorded in a laboratory notebook. An example TCLP Analysis Record is presented as Figure 2.

A summary of required calculations for this method follows:

$$10.1 \quad \% \text{ Solids} = \frac{\text{Weight of the Solid}}{\text{Total Weight of Waste}} \times 100$$

$$10.2 \quad \% \text{ Dry Solids} = \frac{\text{Weight of Waste and Filters} - \text{Tared Weight of Filters}}{\text{Initial Weight of Waste}} \times 100$$

$$10.3 \quad \text{Weight of Waste to Charge ZHE} = \frac{25 \text{ g}}{\% \text{ Solids}} \times 100$$



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- 10.4 Matrix spike recoveries are calculated by the following formula:

$$\%R (\% \text{ Recovery}) = 100 (X_s - X_u) / K$$

Where:

X_s = measured value for the spiked sample

X_u = measured value for the unspiked sample

K = known value of the spike in the sample

- 10.5 Matrix spike recoveries will be used by the client to correct measured values for analytical bias. The laboratory will provide the uncorrected values and the respective recoveries to the client, for calculation using the following formula:

$$\text{Corrected Value} = 100(X)/\%R$$

Where: X = measured value of the unspiked sample, and
 $\%R$ = matrix spike recovery

- 10.6 Calculation to determine a volume-weighted average concentration when individual phases are analyzed separately (i.e., TCLP extracts are not miscible):

$$\text{Final Analyte Concentration} = \frac{(V_1)(C_1) + (V_2)(C_2)}{V_1 + V_2}$$

Where:

V_1 = volume of the first phase (L)

C_1 = concentration of the analyte of concern in the first phase (mg/L)

V_2 = volume of the second phase (L)

C_2 = concentration of the analyte of concern in the second phase (mg/L)

11.0 QUALITY CONTROL CRITERIA

Minimally, for each extraction batch or maximum of 20 samples extracted, a blank (hereafter referenced as leachate blank) and sample duplicate are also extracted. The duplicate will be used to provide the additional leachate volume needed to perform the TCLP-required matrix spike. See Table 3 for Agency and client specific QC requirements outside this minimal specification, to ensure enough leachate is available for all required analyses and QC.



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- 11.1 The leachate blank for the non-volatile extract is two liters of the same extraction fluid used for the samples run through the procedure. A leachate blank must be prepared for each type of fluid used per batch; therefore, if both extraction fluids are used, two leachate blanks must be analyzed.
- 11.2 A matrix spike including all target analytes (except toxaphene) shall be performed for each waste type, but minimally one matrix spike must be included for each analytical batch. Exceptions to spiking all target analytes may be specified in the Project Profile, depending on the basis for the TCLP request (see also Section 3.0).
- 11.2.1 Exception to spiking each sample type: if the result exceeds the regulatory level and the data is being used solely to demonstrate that the waste property exceeds the regulatory level. This information needs to be provided by the client prior to extraction, if applicable.
- 11.2.2 The breakdown for matrix type includes wastewater treatment sludge, sandy soil, loamy soil, etc., per client. Note this is a more detailed matrix evaluation than the general water and soil options.
- 11.2.3 As a minimum, follow the matrix spike addition guidance provided in each analytical method.
- 11.2.4 Matrix spikes are to be added after filtration of the TCLP extract and before preservation. Matrix spikes should not be added prior to TCLP extraction of the sample.
- 11.2.5 In most cases, matrix spikes should be added at a concentration equivalent to the corresponding regulatory level. If the analyte concentration is less than one half the regulatory level, the spike concentration may be as low as one half of the analyte concentration, but may not be not less than five times the method detection limit. In order to avoid differences in matrix effects, the matrix spikes must be added to the same nominal volume of TCLP extract as that which was analyzed for the unspiked sample.
- 11.2.6 Purpose of the matrix spike is to monitor the performance of the analytical methods used, and to determine whether



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matrix interferences exist. It is important to be meticulous in the preparation and analysis of the matrix spike, as all measured values in the investigative samples will be corrected to reflect the bias determined by the matrix spike. Use of other internal calibration methods, modification of the analytical methods, or use of alternate analytical methods may be needed to accurately measure the analyte concentration of the TCLP extract when the recovery of the matrix spike is below the expected analytical method performance.

- 11.3 All quality control measures described in the appropriate analytical methods shall be followed.

12.0 CORRECTIVE ACTION

Since this is a sample preparation protocol, most problems associated with the extraction will not be evident until the leachates are analyzed. Corrective action for poor leachate blank results will require all samples in the set to be re-prepared.

13.0 HEALTH AND SAFETY

- 13.1 General laboratory safety practices should always be followed. Waste samples should be handled with care due to the uncertainty of the properties and contents involved. Refer to the specific MSDS for the hazardous properties of any chemical or reagent involved in this procedure.
- 13.2 Acids should be handled with care.
- 13.3 Since all samples that are being tested may contain hazardous substances, care should be taken to avoid contact with the samples or the filtrates.
- 13.4 Fully fastened lab coat, safety glasses and latex gloves must be worn.
- 13.5 When extracting a known hazardous waste (e.g., radiation, cyanide, or arsenic) the entire extraction apparatus must be placed in a ventilation hood.
- 13.6 Immediately clean up any materials spilled on the floor, in hoods or on bench tops.
- 13.7 All chemical containers should be clean and properly



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labeled.

- 13.8. All damaged or broken glassware should be discarded immediately.
- 13.9 Use caution when disassembling the zero headspace extractor. Do not attempt to operate without receiving proper instructions. (Danger of explosion!)
- 13.10 When performing percent solids, caution should be taken to ensure that the subject solid will not flash upon heating. It is recommended that the drying oven be vented to a hood or other appropriate device.

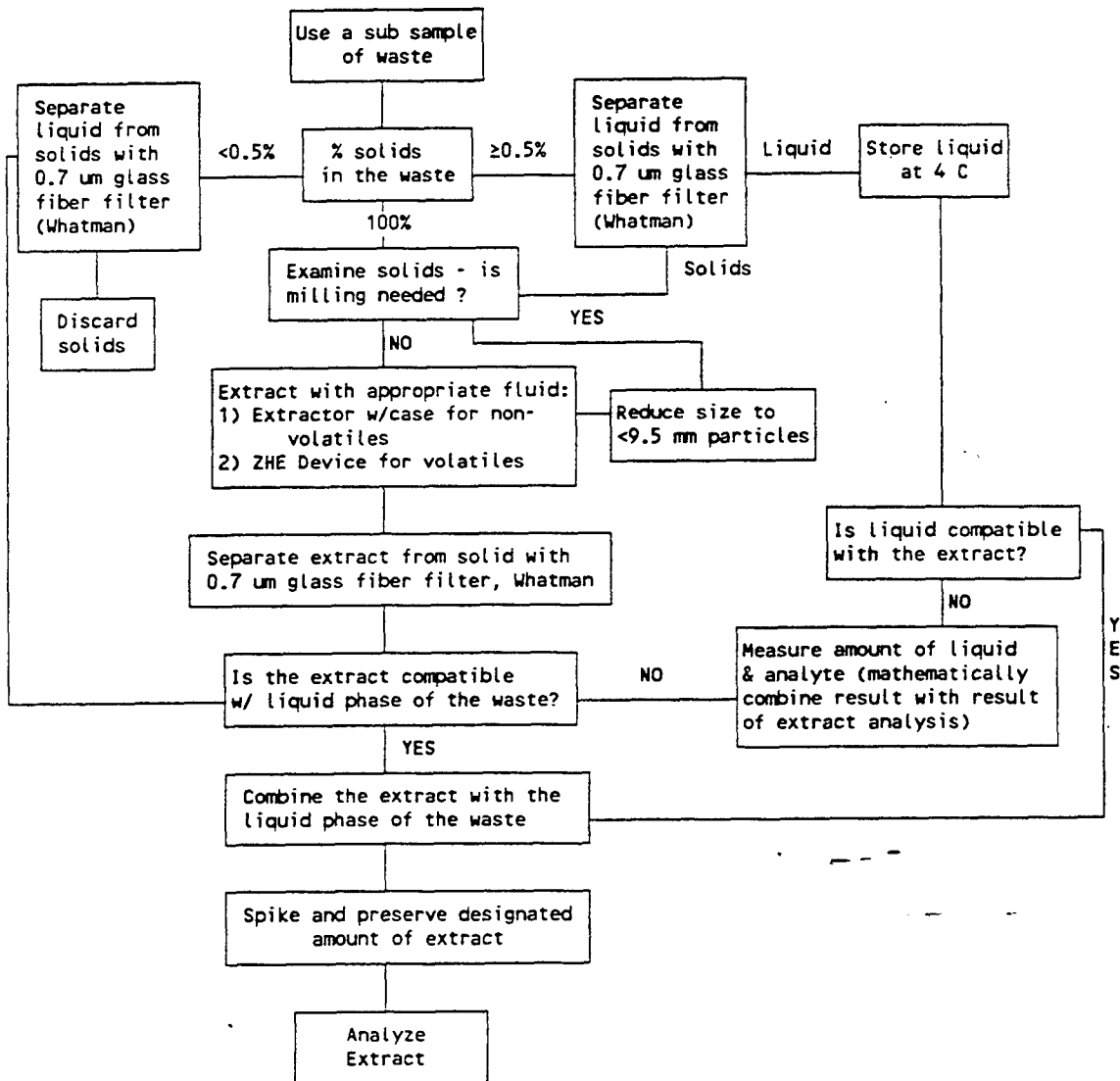


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FIGURE 1. TCLP FLOWCHART



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FIGURE 2. TCLP ANALYSIS LOG

<div style="display: flex; justify-content: space-between;"> WESTON <div style="text-align: center;"> TCLP EXTRACTION DATA (NON-VOLATILE) </div> <div style="text-align: right;"> LOGBOOK # _____ BATCH # _____ </div> </div>	
RFW # _____ CLIENT ID # _____ TCLP ROTATOR BOX # _____ pH AFTER 5 MIN. _____ pH AFTER ACID/HEAT _____ EXTRACTION FLUID _____ WT. OF SAMPLE _____ mL OF EXTRACTION FLUID _____ pH AFTER EXTRACTION _____	INITIAL FILTRATION DATA AND COMMENTS: INITIAL FILTRATE ADDED _____
RFW # _____ CLIENT ID # _____ TCLP ROTATOR BOX # _____ pH AFTER 5 MIN. _____ pH AFTER ACID/HEAT _____ EXTRACTION FLUID _____ WT. OF SAMPLE _____ mL OF EXTRACTION FLUID _____ pH AFTER EXTRACTION _____	INITIAL FILTRATION DATA AND COMMENTS: INITIAL FILTRATE ADDED _____
RFW # _____ CLIENT ID # _____ TCLP ROTATOR BOX # _____ pH AFTER 5 MIN. _____ pH AFTER ACID/HEAT _____ EXTRACTION FLUID _____ WT. OF SAMPLE _____ mL OF EXTRACTION FLUID _____ pH AFTER EXTRACTION _____	INITIAL FILTRATION DATA AND COMMENTS: INITIAL FILTRATE ADDED _____
RFW # _____ CLIENT ID # _____ TCLP ROTATOR BOX # _____ pH AFTER 5 MIN. _____ pH AFTER ACID/HEAT _____ EXTRACTION FLUID _____ WT. OF SAMPLE _____ mL OF EXTRACTION FLUID _____ pH AFTER EXTRACTION _____	INITIAL FILTRATION DATA AND COMMENTS: INITIAL FILTRATE ADDED _____
EXTRACTION(S) DATES AND TIMES: START: _____ ANALYST _____ END: _____ ANALYST _____	CALCULATION: $\frac{R_2 \times V_3 \times V_1}{R_1 \times V_2} = X$ WHERE: R_1 = Wt. of residue obtained through initial filtration R_2 = Wt. of residue used for extraction V_1 = Initial vol. of liquid obtained through initial filtration V_2 = Volume of extraction fluid used for extraction V_3 = Volume obtained from extraction after filtration X = Volume of initial filtrate (V_1) to be added to V_2

Reviewed by/Date:

RFW 21-21-001/F-08/91

Page:

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FIGURE 3: TCLP LAB SPIKING DATA RECORD (METALS)

(See also Appendix I)

TCLP-1

Source #: _____
 500 ug/mL each: As, Cr, Pb, Ag
 100 ug/mL each: Cd, Se
 20 ug/mL each: Hg

Lot #: _____
Expiration Date: _____

TCLP-2

Source #: _____
10,000 ug/mL Ba

Lot #: _____
Expiration Date: _____

[illegible]



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TABLE 1. TOXICITY CHARACTERISTIC CONSTITUENTS AND REGULATORY LEVELS

EPA HW Number ¹	Constituent	CAS No. ²	Regulatory Level (mg/L)
D004	Arsenic	7440-38-2	5.0
D005	Barium	7440-39-3	100.0
D018	Benzene	71-43-2	0.5
D006	Cadmium	7440-43-9	1.0
D019	Carbon Tetrachloride	56-23-5	0.5
D020	Chlordane	57-74-9	0.03
D021	Chlorobenzene	108-90-7	100.0
D022	Chloroform	67-66-3	6.0
D007	Chromium	7440-47-3	5.0
D023	o-Cresol	95-48-7	³ 200.0
D024	m-Cresol	108-39-4	³ 200.0
D025	p-Cresol	108-44-5	³ 200.0
D026	Cresol		³ 200.0
D016	2,4-D	94-75-7	10.0
D027	1,4-Dichlorobenzene	106-46-7	7.5
D028	1,2-Dichloroethane	107-06-2	0.5
D029	1,1-Dichloroethylene	75-35-4	0.7
D030	2,4-Dinitrotoluene	121-14-2	³ 0.13
D012	Endrin	72-20-8	0.02
D013	Heptachlor (and its epoxides)	76-44-8	0.008
D032	Hexachlorobenzene	118-74-1	³ 0.13
D033	Hexachloro-1,3-butadiene	87-68-3	0.5
D034	Hexachloroethane	67-72-1	3.0
D008	Lead	7439-92-1	5.0
D013	Lindane	58-89-9	0.4
D004	Mercury	7439-97-6	0.2
D014	Methoxychlor	72-43-5	10.0
D035	Methyl ethyl Ketone	78-93-3	200.0
D036	Nitrobenzene	98-95-3	2.0
D037	Pentachlorophenol	87-86-5	100.0
D038	Pyridine	110-86-1	³ 5.00
D010	Selenium	7782-49-2	1.0
D011	Silver	7740-22-4	5.0
D039	Tetrachloroethylene	127-18-4	0.7
D015	Toxaphene	9001-35-2	0.5
D040	Trichloroethylene	79-01-6	0.5
D041	2,4,5-Trichlorophenol	95-95-4	400.0
D042	2,4,6-Trichlorophenol	88-06-2	2.0
D017	2,4,5-TP (Silvex)	93-72-1	1.0
D043	Vinyl Chloride	75-01-4	0.2

¹ Hazardous waste number

² Chemical abstracts service number

³ Quantitation limit is greater than the calculated regulatory level. The quantitation limit therefore becomes the regulatory level.

⁴ If o-, m-, p-cresol concentration cannot be differentiated, the total cresol (D026) concentration is used. The regulatory level for total cresol is 200 mg/L



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TABLE 2. SAMPLE MAXIMUM HOLDING TIMES

	From: Field Collection To: TCLP Extraction	From: TCLP Extraction To: Preparative Extraction	From: Preparative Extraction To: Determinative Analysis	Total Elapsed Time
Volatiles	14 days	NA	14 days	28 days
Semivolatiles	14 days	7 days	40 days	54 days
Mercury	28 days	NA	28 days	56 days
Metals, except Mercury	180 days	NA	180 days	360 days
NA = Not Applicable				

TABLE 3. SPECIFIC AGENCY AND CLIENT REQUIREMENTS

AGENCY/CLIENT	TYPE QC REQUIRED: LB, MS, MSD, DUP, ETC. (LB = leachate blank)	FREQUENCY OF QC	COMMENTS/SPECIAL INSTRUCTIONS
EPA Region V	<ul style="list-style-type: none">• LB• MS	<ul style="list-style-type: none">• 1 per extraction batch of ≤ 20• every sample	
EPA Region II	<ul style="list-style-type: none">• LB• MS	<ul style="list-style-type: none">• 1 per extraction batch of ≤ 20• 1 per sample type	QC is also dependent on use of data and method chosen. For example, if CLP is required, a MS/MSD (organic) and MS/DUP (inorganic) would need to be analyzed.



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TCLP: NON-VOLATILE

Eff. Date: 03/15/91 Initiated By: Dianne S. Therry Approved By: Jack R. Tuschall Authorized By: Marty J. Volandt SP No. 21-15-1311.1

APPENDIX 1: TCLP METALS SPIKING

The purpose of the matrix spike is to monitor the performance of the analytical methods used and to determine whether matrix interferences exist.

Matrix spikes are to be added after filtration of the TCLP extract and before preservation. Matrix spikes should not be added prior to the TCLP extraction of the sample.

In order to avoid differences in matrix effects, the matrix spikes must be added to the same nominal volume of the TCLP extract as that which was analyzed for the unspiked sample.

The following steps detail the TCLP metals spiking procedure:

1. Measure out 100 mL of TCLP extract and transfer it into a small container.
2. Using an Eppendorf pipet, dispense 1 mL of each standard, TCLP-1 and TCLP-2, into the TCLP extract.
3. Preserve the TCLP spiked extract with 2 mL of concentrated nitric acid.
4. Store at 4°C.

METALS DIGESTION: AQUEOUS SAMPLES BY ICP/AA FLAME
(OP NO. 21-15-3020.1)

Amendments to SOP of Method 3020 (SOP #21-15-3020.1)

1. All metals listed in Table 8-4 of QA Plan except mercury will be performed by ICP.
2. MS/duplicate data will be used to assess accuracy and precision for metals.

INORGANIC ANALYSIS PROTOCOL
METALS DIGESTION: AQUEOUS SAMPLES BY ICP/AA FLAME

1.0 PURPOSE

- 1.1 This method describes a technique for the preparation of aqueous samples for the determination of trace elements in solution by ICP or AA Flame.

2.0 SCOPE AND APPLICATION

- 2.1 This method describes an acceptable sample preparation procedure for "total" element analysis; the procedure is a total recoverable acid solubilization procedure. Note: the ICP/flame AA digest is used for the determination of Sb by GFAA.

3.0 PRESERVATION AND HOLDING TIME

- 3.1 For the determination of total or total recoverable elements, the sample is acidified with (1+1) HNO_3 to pH 2 or less as soon as possible, preferably at the time of collection.
- 3.2 The holding time is 180 days.

4.0 INTERFERENCES

- 4.1 For the determination of trace elements, contamination and loss are of prime concern. Dust in the laboratory environment, impurities in reagents, and impurities on laboratory apparatus are all sources of potential contamination. The collection and treatment of the sample requires particular attention to laboratory glassware, which should be thoroughly washed with detergent and tap water; rinsed with (1+1) nitric acid, tap water, (1+1) hydrochloric acid, tap water, and finally deionized, distilled water in that order. (Refer to OP 21-20-014).

5.0 APPARATUS

- 5.1 150 mL Griffin beakers, watch glasses, graduated cylinders, hot plate, funnels, filter paper (Whatman 42), thermometer (0-200°C).

6.0 REAGENTS

- 6.1 Hydrochloric acid conc. (sp gr 1.19).

METALS DIGESTION: SOIL SAMPLES (SP NO. 21-15-3050.1)

- 6.2 Nitric acid conc. (sp gr 1.41).
- 6.3 Hydrogen peroxide (30%).
- 6.4 Deionized water, ASTM Type II from Milli-Q system (Q-water).
- 6.5 2% HNO₃ (V/V), 2 mL conc HNO₃ per 100 mL Q-water.
- 6.6 Laboratory control stock solutions. Refer to OP 21-15-3000.4.
- 6.7 Mixed calibration standard solutions. Refer to OP 21-15-3000.4.
- 7.0 PROCEDURE
- 7.1 ICP/Flame AA Digestion
 - 7.1.1 Shake sample vigorously to achieve homogeneity.
 - 7.1.2 Using universal litmus paper, check pH. Note if greater than pH 2 in the digestion notebook and complete/distribute a sample discrepancy report.
 - 7.1.3 Pour 100 mL of sample into graduated cylinder then transfer into a 250 mL pyrex beaker.
 - 7.1.4 Add 2 mL 1:1 HNO₃; add 10 mL 1:1 HCl.
 - 7.1.5 Cover with a watch glass and heat until volume is less than 50 mL (Do not boil, do not reduce to less than 25 mL).
 - 7.1.6 Cool sample, filter through Whatman 42 paper into a graduated cylinder, dilute to 100 mL with deionized water. Sample is now ready for analysis. Document sample appearance, and preparation information in digestion notebook.
- 7.2 GFAA Digestion
 - 7.2.1 Shake sample vigorously to achieve homogeneity.
 - 7.2.2 Using universal litmus paper, check pH. Note if greater than pH 2.
 - 7.2.3 Pour 100 mL of sample into graduated cylinder, then transfer into a 250 mL pyrex beaker.
 - 7.2.4 Add 1 mL 1:1 HNO₃; add 2 mL 30% H₂O₂.
 - 7.2.5 Cover with a watch glass and heat until volume is less than 50 mL (do not boil, do not reduce to less than 25 mL).

7.2.6 Cool sample, filter through Whatman 42 paper into a graduated cylinder, dilute to 100 mL with deionized water. Sample is now ready for analysis. Document sample appearance and preparation information in the digestion notebook.

8.0 QUALITY CONTROL

8.1 Method Blank

8.1.1 A minimum of one method blank, consisting of deionized water must be processed through each sample preparation procedure for each batch of samples digested or each group of 20 samples, whichever is more frequent.

8.2 Laboratory Control Sample

8.2.1 Duplicate laboratory control samples must be processed through each sample preparation procedure for each batch of samples digested or each group of 20 samples, whichever is more frequent.

8.3 Matrix Spike Samples are analyzed as requested by the client.

8.4 Duplicate Samples are analyzed as requested by the client.

9.0 METHOD PERFORMANCE

9.1 Laboratory control charts are maintained for laboratory control standards. Accuracy and precision is based on the laboratory control standards.

10.0 REFERENCE

10.1 SOW 788, Revision 2/89.

11.0 SAFETY

Fully fastened labcoat, safety glasses and latex gloves should be worn. All damaged or broken glass should be discarded immediately. All chemical containers should be clean and properly labeled. Immediately cleanup any materials spilled on the floor, in hoods, or on bench tops.



ANALYTICS DIVISION
STANDARD PRACTICES
MANUAL
COMPANY CONFIDENTIAL AND PROPRIETARY

OPERATING PRACTICE
METALS DIGESTION
SOIL SAMPLES

Eff. Date: 10/19/90 Initiated By: Dianne S. Therry Approved By: Jack R. Tuschall Authorized By: Marty J. Volandt SP No. 21-15-3050.1

INORGANIC ANALYSIS PROTOCOL
METALS DIGESTION: SOIL SAMPLES

These Approval Signatures Are Kept on File
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REVISION NUMBER: 02

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Revision 01: 12/01/89
Revision 02: 10/26/90

Reasons for Change:

• format changes



ANALYTICS DIVISION
**STANDARD PRACTICES
MANUAL**
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**OPERATING PRACTICE
METALS DIGESTION
SOIL SAMPLES**

Eff. Date: 10/19/90 Initiated By: Dianne S. Therry Approved By: Jack R. Fuschall Authorized By: Marty J. Vollandt SP No. 21-15-3050.1

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REVISION NUMBER: 02

1.0 PURPOSE

- 1.1 This method describes a technique for the preparation of soils/sediments for the determination of trace elements in solution by ICP or AA.

2.0 SCOPE AND APPLICATION

- 2.1 This method describes an acceptable sample preparation procedure for "total" element analysis. The procedure is a nitric acid digestion.
- 2.2 The preparation procedures for GFAA and ICP digests differ slightly in the final steps. HCl is used as the final acid for flame AA and ICP preparations. The ICP digest is also used for the determination of Sb by GFAA.

3.0 REFERENCE

- 3.1 SOW (788), Revision 2/89.

4.0 PRESERVATION AND HOLDING TIME

- 4.1 Soil/sediment (non aqueous) samples must be refrigerated at 4°C ($\pm 20^\circ$) from receipt until analysis.
- 4.2 Holding times have not been established by the U.S. EPA for soil samples. However, the aqueous sample holding time of 180 days is used as a guideline.



ANALYTICS DIVISION

STANDARD PRACTICES

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OPERATING PRACTICE

METALS DIGESTION

SOIL SAMPLES

Eff. Date: 10/19/90 Initiated By: Dianne S. Therry Approved By: Jack R. Tuschall Authorized By: Marty J. Vollandt SP No. 21-15-3050.1

5.0 INTERFERENCES

- 5.1 For the determination of trace elements, contamination and loss are of prime concern. Dust in the laboratory environment, impurities in reagents, and impurities on laboratory apparatus are all sources of potential contamination. The collection and treatment of the sample requires particular attention to laboratory glassware, which should be thoroughly washed with detergent and tap water; rinsed with (1+1) nitric acid, tap water, (1+1) hydrochloric acid, tap water, and finally deionized, distilled water in that order. (See SP 21-20-014).

6.0 APPARATUS

- 6.1 250 mL Griffen beakers, watch glasses, graduated cylinders, hot plate, funnels, filter paper (Whatman 42), thermometer (0°-200°C).

7.0 REAGENTS

- 7.1 Hydrochloric acid conc. (sp gr 1.19).
- 7.2 Nitric acid conc. (sp gr 1.41).
- 7.3 Hydrogen peroxide (30%).
- 7.4 Deionized water, ASTM Type II from Milli-Q System (Q-water).
- 7.5 2% HNO_3 (v/v), 2 mL conc. HNO_3 per 100 mL Q-water.
- 7.6 Laboratory control stock solutions. - Refer to SP 21-15-3000.2.
- 7.7 Mixed calibration standard solutions. Refer to SP 21-15-3000.2.

8.0 PROCEDURE

- 8.1 Mix sample thoroughly.
- 8.2 Weigh 1.0 to 1.5 grams of sample into pyrex beaker. Record weight to the nearest 0.01g (Figure A).



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OPERATING PRACTICE
METALS DIGESTION
SOIL SAMPLES

Eff. Date: 10/19/90 Initiated By: Dianne S. Therrv Approved By: Jack R. Tuschall Authorized By: Marty J. Vollandt SP No. 21-15-3050.1

- 8.3 Add 10 mL 1:1 HNO_3 , mix the slurry, cover with a watch glass and heat the sample to 95°C. Reflux for 10 minutes. Do not boil.
- 8.4 Allow to cool and add 5 mL concentrated HNO_3 . Replace the watch glass and reflux for 30 minutes. Do not boil, do not reduce to less than 5 mL.
- 8.5 Allow to cool. Add 2 mL of Q-water and 3 mL H_2O_2 (30%). Warm until reaction stops.
- 8.6 Continue to add 1 mL aliquots of H_2O_2 until the effervescence is minimal or until the sample appearance is unchanged. Do not add more than a total of 10 mL H_2O_2 .
- 8.7 If sample is being prepared for furance (AA) analysis, reduce sample volume to approximately 2 mL, add 10 mL of Q-water and warm.
- 8.8 If sample is being prepared for ICP analysis, add 10 mL of Q-water, and 5 mL 1:1 HCL and heat for an additional 10 minutes.
- 8.9 Cool samples and filter through Whatman No. 42 filter paper. Rinse digestion beaker with several aliquots of 2% HNO_3 . Pour rinsates through filter paper. Dilute sample to 200 mL sample volume with acidified water (2% HNO_3 v/v) to maintain constant acid strength. Sample is now ready for analysis.
- 8.10 Document on Figure A all preparation steps as per OP 21-15-3000.3.
- 9.0 QUALITY CONTROL
- 9.1 Method Blank
- 9.1.1 A minimum of one method blank, consisting of deionized water must be processed through each sample preparation procedure for each batch of samples digested or each group of 20 samples, whichever is more frequent.
- 9.2 Laboratory Control Sample



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STANDARD PRACTICES
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OPERATING PRACTICE
METALS DIGESTION
SOIL SAMPLES

Eff. Date: 10/19/90 Initiated By: Dianne S. Therry Approved By: Jack R. Tuschall Authorized By: Marty J. Vollandt SP No. 21-15-3050.1

9.2.1 Duplicate laboratory control samples must be processed through each sample preparation procedure for each batch of samples digested or each group of 20 samples, whichever is more frequent.

9.3 Matrix Spike Samples are analyzed as requested by the client.

9.4 Duplicate Samples are analyzed as requested by the client.

10.0 METHOD PERFORMANCE

10.1 Laboratory control charts are maintained for laboratory control standards. Accuracy and precision is based on the laboratory control standards.

11.0 SAFETY

Fully fastened labcoat, safety glasses and latex gloves must be worn.

All chemical containers should be clean and properly labeled.

Immediately cleanup any materials spilled on the floor, in hoods, or on bench tops.

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OPERATING PRACTICE

METALS DIGESTION

SOIL SAMPLES

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Figure A
METAL DIGESTION LOG

[illegible]

COMMENTS:

REVIEWED BY _____

RFW# 21-21-001/C-03/P1

METALS BY ICP (OP NO. 21-15-0200.7)

Amendments to SOP of Method 0200.7 (SOP #21-15-0200.7)

1. An MS/dup will be required in the TCLP leachate for metals. MS data will be used to assess accuracy for metals. Sample duplicate and MS QC data will be reported.
2. TCLP metals using the associated detection limits will be evaluated.
3. The exemptions to the control limits for Ag are in accordance with the Inorganic CLP (3/90 SOW), Page E-19, Section 8, Paragraph 3.
4. Control limits will be +/- 20% RPD for sample replicates. Data will be flagged if these limits are exceeded.
5. The units for Table II are ug/L.
6. The target analytes on Table I are silver, lead, chromium, cadmium, barium, arsenic, and selenium. The target analytes on Table II are arsenic, barium, cadmium, chromium, lead, selenium, and silver.
7. The following elements interfere with target analytes:

Target ElementElements that Interfere

Chromium
Selenium
Arsenic
Barium
Cadmium
Lead
Silver

Iron, vanadium
Magnesium, iron, vanadium
Aluminum, chromium, iron, vanadium
None
Arsenic
Iron, aluminum, magnesium
Iron, vanadium

INORGANIC ANALYSIS PROTOCOL
METALS BY ICP

1.0 PURPOSE

Determination of elements by Inductively Coupled Plasma Atomic Emission Spectrophotometry in aqueous media.

2.0 REFERENCE

2.1 EPA-600/4-79-020, Methods for Chemical Analysis of Water and Wastes, March 1979, Method 200.7.

2.2 U.S. EPA CLP SOW 788, Method 200.7 CLP-M.

3.0 PRINCIPLE

The basis of the method is the measurement of atomic emission by an optical spectroscopic technique. Samples are nebulized and the aerosol that is produced is transported to the plasma torch where excitation occurs. Characteristic atomic-line emission spectra are produced by a radio-frequency inductively coupled plasma (ICP). The spectra are dispersed by a grating spectrometer and the intensities of the line are monitored by photomultiplier tube.

4.0 INTERFERENCES

Several types of interference effects may contribute to the inaccuracies in the determination of trace elements.

4.1 Spectral Interferences

Spectral Interferences can be corrected for via computer application of interelement correction factors and/or background correction.

4.2 Physical Interferences

Generally, physical interferences are considered to be effects associated with the sample nebulization and transport processes. These interferences can be reduced by dilution of the sample and/or utilization of standard addition techniques. Samples with high dissolved solids content often exhibit inaccuracies attributable to this type of interference.

4.3 Chemical Interferences

Chemical Interferences are characterized by molecular compound formation and ionization effects. Matrix matching and standard addition procedures can compensate for this interference.

5.0 METHOD DETECTION LIMIT

Refer to Table I.

6.0 OPTIMUM CONCENTRATION RANGE

Refer to Table I for linear range information.

7.0 REAGENTS

7.1 Nitric Acid, conc.

7.2 Nitric Acid, (1+1): Add 500 mL conc. HNO_3 to 400 mL deionized water and dilute to 1 liter. Hydrochloric Acid (1+1): Add 500 mL conc. HCl to 400 mL deionized water and dilute to 1 liter.

7.3 Deionized water, ASTM Type II reagent grade.

8.0 STANDARDS

Custom-made standards: Inorganic Ventures (Refer to Table I.)

8.1 Calibration Standards

RFWCAL 1, 2, 3, 4A, 4B. Add 1 mL of stock, 1 mL 1+1 HNO_3 , 2.5 mL 1+1 HCl to 50 mL deionized water and dilute to 100 mL.

8.2 Continuing Calibration Verification Standards

RFWICV 1, 2, 3, 4A, 4B. Add 1 mL of stock, 1 mL 1+1 HNO_3 , 2.5 mL 1+1 HCl to 50 mL deionized water and dilute to 100 mL.

8.3 CRI (low concentration verification standard)

Add 2 mL of each calibration standard (RFWCAL), 1 mL 1+1 HNO_3 , 2.5 mL HCl to 50 mL of deionized water and dilute to 100 mL.

8.4 Interferent Check Standard A

Check-2. Add 10 mL of stock check-2, 1 mL 1+1 HNO_3 , 2.5 mL HCl , to 50 mL deionized water and dilute to 100 mL.

8.5 Interferent Check Standard B

Check-1,2. Add 10 mL of stock check-2, 1 mL check-1, 1 mL 1+1 HNO_3 , 2.5 mL 1+1 HCl to 50 mL deionized water and dilute to 100 mL.

8.6 Calibration Blank

Add 15 mL 1+1 HNO_3 , 5 mL 1+1 HCl to 100 mL of deionized water and dilute to 200 mL.

9.0 INSTRUMENT PARAMETERS

Refer to Table II for wavelengths.

10.0 PROCEDURE

Refer to ICP Operation SOP (OP# 21-15-6000.1) for specific procedural information.

11.0 QUALITY CONTROL

Table II illustrates the required QC, control criteria and proper corrective actions.

11.1 Calibration must be performed daily with a blank and a high standard. (Multiple level standards are analyzed quarterly. Refer to 11.9.)

11.2 Calibration must be verified with a mid-range check standard (ICV) prepared independently from the calibration standard. The ICV must not vary more than 10% from the true value.

11.3 Calibration verification will be performed with a calibration blank (CCB) and check standard (CCV) after every 10 samples and at the end of the analysis. The CCV must not vary more than 10% from the true value.

11.4 A low level calibration verification standard (CRI) must be analyzed at the beginning and end of the analytical run to document the linearity of response at the detection limit. The standard should be at a level of 2 times the CRDL.

11.5 An interference check standard (ICS) must be analyzed at the beginning and end of the analytical run to document the accuracy of the interelement corrections.

11.6 Dilute samples if they exceed the quarterly determined linear range.

11.7 Preparation quality control samples (i.e. method blanks, laboratory control standards, matrix spikes and duplicates) must accompany any sample batches processed through digestion or preparation procedures as described in the Quality Assurance Project Plan.

11.8 Specific, additional QC requirements may be necessary for individual clients. Refer to the appropriate source for this information (eg. SOW 788 for USEPA CLP).

11.9 Refer to OP# 21-15-005.1 for a description of quarterly QC procedures (i.e. IDL, IEC and Linear Range determinations and quarterly 5 pt. calibrations).

12.0 **CALCULATION**

All calculations are performed directly by the instrument data system. The laboratory information system (LIMS) converts all instrument concentrations to the appropriate reporting units.

13.0 **METHOD PERFORMANCE**

Laboratory control charts will be maintained for blanks and laboratory control standards. Accuracy and precision will be based on the laboratory control standards.

14.0 **ANALYSIS RATE**

Instrument set-up and calibration can occur in 1 hour. Samples are subsequently analyzed at a rate of 15-20 samples per hour.

15.0 **SAFETY**

Safety glasses must be worn when handling standards or samples.

Table II. Wave Length Instrument Detection Limits (MDL)
Standard Laboratory Reporting Limits (LRL), and Limits Range

ELEMENT	WAVE LENGTH (nm)	APPROXIMATE IDL(ug/L)	REPORTING LIMIT (ug/L)	OPTIMUM CONC. RANGE ug/L
Aluminum	308.215	30	200	200 --> 100,000
Barium	455.403	3	200	200 --> 200,000
Beryllium	313.042	0.1	5	5.0 --> 2,500
Cadmium	226.502	2	5	5.0 --> 2,500
Chromium	267.716	3	10	5.0 --> 2,500
Cobalt	228.626	3	50	10 --> 5,000
Copper	324.754	2	25	25 --> 25,000
Iron	259.940	11	100	100 --> 200,000
Manganese	257.610	0.6	15	15 --> 7,500
Nickel	231.604	5	40	40 --> 20,000
Silver	318.068	5	10	10 --> 10,000
Vanadium	292.402	4	50	50 --> 10,000
Zinc	213.856	1	20	20 --> 10,000
Calcium	317.933	34	5000	500 --> 500,000
Sodium	588.995	18	500	500 --> 500,000
Potassium	766.491	421	5000	500 --> 500,000
Magnesium	279.079	26	5000	500 --> 500,000
Arsenic	193.696	28	120	100 --> 40,000
Selenium	196.026	75	300	100 --> 40,000
Lead	220.353	16	100	100 --> 25,000
Thallium	190.864	41	160	100 --> 20,000
Titanium	334.941	50	100	50 --> 20,000
Strontium	407.771	50	100	50 --> 20,000
Boron	249.773	50	100	50 --> 20,000
Molybdenum	202.030	50	100	50 --> 20,000
Antimony	206.833	35	60	50 --> 40,000
Silicon(SiO ₂)	251.612	50	100	50 --> 20,000
Tin	189.900	50	100	50 --> 20,000
Lithium	670.784	50	100	50 --> 40,000
Uranium	367.007	1000	1000	1000 --> 10,000
Scandium	361.384	50	100	50 --> 5,000

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Table III. Quality Control Limits and Corrective Actions

QC SAMPLE	IDENTIFICATION	FREQUENCY	CONTROL LIMITS	ACTION TO TAKE IF OUT-OF-CONTROL
MB	Method Blank	5† 1 Per 20 samples digested	< CRDL	Notify Section Management; Redigest
LCS	Laboratory Control Standard	5† 1 Per 20 samples digested	80†-120† Ex: Sb, Ag	Notify Section Management; Redigest
ICV	Initial Calibration Verification Std	Once Immediately after ICV	< CRDL	Recalibrate
ICB	Initial Calibration Blank	Once Immediately After Calibration	90-110†	Recalibrate
CCV	Continuing Calibration Verification Std	10† After Every CCV	< CRDL	Recalibrate; Rerun Previous 10 Samples
CCB	Continuing Calibration Blank	10† After Every 10 Samples	90-110†	Recalibrate; Rerun Previous 10 Samples
CRI	Low Concentration Check Standard	Analyze Twice 1-After Calibration 2-At End of Run	None	None
ICS	Interference Check Standard	Analyze Twice 1-After calibration 2- At End of Run	80†-120†	Recalibrate
S. Dil.	Serial Dilution	5† 1 Per 20 Sample Received (Matrix)	90†-110†	None

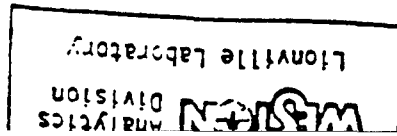
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Table III. Quality Control Limits and Corrective Actions

QC SAMPLE	IDENTIFICATION	FREQUENCY	CONTROL LIMITS	ACTION TO TAKE IF OUT-OF-CONTROL
S	Spike Sample	5 ± 1 Per 20 samples received	75±-125±	PMS at 2 X CRDL or 2X SR whichever is greater
R	Replicate Sample	5 ± 1 Per 20 samples received	*	None
PMS	Post Matrix Spike	Analyze when Spike is Out- Of-Control	--	None

*SR>5X CRDL = 20± RPD
SR<5X CRDL = ±CRDL

SR = Sample Result

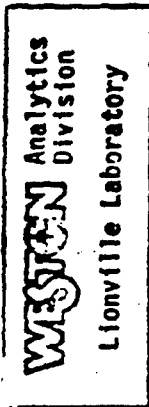


ICV/LCS Solution

ELEMENT	STD. ID.	STOCK		FINAL	
		CONCENTRATION UG/L		CONCENTRATION (UG/L)	
Aluminum	RFW ICV-2	1000		10,000	
Antimony	RFW ICV-3	300		3,000	
Arsenic	RFW ICV-4A	1000		10,000	
Barium	RFW ICV-2	1000		10,000	
Beryllium	RFW ICV-1	25		25	
Cadmium	RFW ICV-1	25		250	
Calcium	RFW CLP-1	2500		25000	
Chromium	RFW ICV-1	50		500	
Cobalt	RFW ICV-1	250		2500	
Copper	RFW ICV-1	125		1250	
Iron	RFW ICV-1	500		5000	
Lead	RFW ICV-1	250		2500	
Magnesium	RFW CLP-1	2500		25000	
Manganese	RFW ICV-1	75		750	
Nickel	RFW ICV-1	200		2000	
Potassium	RFW CLP-1	2500		25000	
Selenium	RFW ICV-4A	1000		10000	
Silver	RFW ICV-1	50		500	
Sodium	RFW CLP-1	25000		25000	
Thallium	RFW ICV-4A	1000		10000	
Vanadium	RFW ICV-1	250		2500	
Zinc	RFW ICV-1	100		1000	
Strontium	RFW ICV-4A	500		5000	
Molybdenum	RFW ICV-4B	500		5000	
Silicon	RFW ICV-4B	500		5000	
Titanium	RFW ICV-4B	500		5000	
Tin	RFW ICV-4B	500		5000	
Boron	RFW ICV-4A	500		5000	

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Standards and CRI for ICP Metals (con't)



RFWCAL1

<u>ELEMENT</u>	<u>STOCK</u> <u>CONCENTRATION UG/ML</u>	<u>FINAL</u> <u>CONCENTRATION (UG/L)</u>	<u>CRI (UG/L)</u>
Beryllium	50	500	10
Cadmium	50	500	10
Chromium	100	1000	20
Cobalt	500	5000	100
Copper	250	2500	50
Iron	1000	10,000	NR
Lead	500	5000	100
Manganese	150	1500	30
Nickel	400	4000	80
Silver	100	1000	20
Vanadium	500	5000	100
Zinc	200	2000	40

RFWCAL2

<u>ELEMENT</u>	<u>STOCK</u> <u>CONCENTRATION UG/ML</u>	<u>FINAL</u> <u>CONCENTRATION (UG/L)</u>	<u>CRI (UG/L)</u>
Sodium	5000	50,000	NR
Potassium	5000	50,000	NR
Calcium	5000	50,000	NR
Magnesium	5000	50,000	NR
Aluminum	1000	10,000	NR
Barium	1000	10,000	NR

RFWCAL3

<u>ELEMENT</u>	<u>STOCK</u> <u>CONCENTRATION UG/ML</u>	<u>FINAL</u> <u>CONCENTRATION (UG/L)</u>	<u>CRI (UG/L)</u>
Antimony	600	6000	120

Table I. Calibration Standards and CRI for ICP Metals (con't)

RFWCAL4A, B

ELEMENT	STOCK		FINAL CONCENTRATION (UG/L)	CRI (UG/L)
	CONCENTRATION UG/ML			
A Arsenic	2000		20,000	400
A Selenium	2000		20,000	400
A Thallium	2000		20,000	400
A Strontium	1000		10,000	-
B Molybdenum	1000		10,000	-
B Silicon	1000		10,000	-
B Titanium	1000		10,000	-
B Tin	1000		10,000	-
A Boron	1000		10,000	-

METALS PREPARATION: MERCURY DIGESTION

(OP-21-15-0245.6)

WESTERN

COPY # : 007
ISSUED TO :

PROPRIETARY INFORMATION
OPERATING PRACTICE
MERCURY DIGESTION

06/19/90

LEO

EMH

MJV

21-15-0245.6

INORGANIC ANALYSIS PROTOCOLS
METALS PREPARATION: MERCURY DIGESTION

1.0 PURPOSE

Preparation of aqueous and nonaqueous samples for mercury analysis.

2.0 REFERENCE

EPA-600/4-79-020, Methods for Chemical Analysis of Water and Wastes, Method 245.1.

U.S. EPA CLP SOW 788.

3.0 PRINCIPLE

Organo-mercury compounds will not respond to the cold vapor AA technique and therefore must be broken down and converted to mercuric ions. These compounds are oxidized by the addition of potassium permanganate and potassium persulfate.

4.0 REAGENTS

4.1 Sulfuric acid, concentrated: Reagent grade.

4.2 Nitric acid, concentrated: Reagent grade.

4.3 Potassium permanganate, 5% solution, prepared by dissolved 50 g of potassium permanganate in 1000 mL of deionized water.

4.4 Potassium persulfate, 5% solution, prepared by dissolving 50 g of potassium persulfate in 1000 mL of deionized water.

5.0 STANDARDS

5.1 Stock mercury solution. Transfer 1 mL of 1000 ppm Hg standard to a 100 mL volumetric flask, add 0.15 mL of concentrated nitric acid and fill to volume with deionized water. 1 mL = 10 ug.

5.2 Intermediate mercury standard solution. Transfer 1 mL of stock mercury solution to a 100 mL volumetric, add 0.15

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mL of concentrated nitric acid and fill to volume with deionized water. 1 mL = 0.1 ug.

5.3 Continuing Calibration Verification Standard (CCV) solution. Transfer 0.250 mL of RFW-3 (400 ug/mL) to a 250 mL volumetric flask, add 0.38 mL of concentrated nitric acid and fill to volume with deionized water. 1 mL = 0.4 ug.

5.4 Working Calibration Standards. Prepare fresh daily. To a series of 300 mL BOD bottles add the indicated aliquots of the Intermediate Standard (5.2). Add sufficient deionized water to achieve a volume of 100 mL in each. Mix thoroughly. Record the bottle number for each sample (see figure 1).

Volume of Intermediate Standard (mL)	Concentration (ug/mL)
0	0
0.2	0.2
0.5	0.5
1.0	1.0
2.0	2.0
5.0	5.0
10.0	10.0
15.0	15.0
20.0	20.0

5.5 Initial Calibration Verification (ICV)/Continuing Calibration Verification (CCV)/Laboratory Control Standard (LCS) Solution. Prepare fresh daily. Prepare ICV, CCV, and LCS solutions. Prepare enough bottles to satisfy the quality control requirements. Transfer 0.5 mL of the CCV solution to each 300 mL BOD bottle. Add sufficient deionized water to bring the volume to 100 mL. Mix thoroughly. Record bottle numbers.

5.6 Method Blank (MB) and Continuing Calibration Blank (CCB). Prepare fresh daily. Prepare CCB and MB. Prepare enough bottles to satisfy the quality control requirements. To each bottle add 100 mL of deionized water. Record bottle numbers.

6.0 PROCEDURE

6.1 Aqueous samples: Transfer 100 mL of sample to a BOD bottle. Record bottle number.

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6.2 Solid samples: Weigh out 0.2 g of soil and transfer to a BOD bottle by washing the weighing dish several times with deionized water into the BOD bottle. Add sufficient deionized water to bring the volume to 100 mL. Record bottle number.

6.3 Digestion: To each bottle prepared above, add 8 mL of potassium permanganate solution, 2.5 mL of nitric acid, 5 mL of sulfuric acid, and 5 mL of potassium persulfate. Stopper each bottle and cover each top with aluminum foil. Autoclave for 15 minutes and allow to cool. Note: Wear elephant hide gloves when removing samples from autoclave. Add acids in a fume hood.

7.0 QUALITY CONTROL

7.1 Method Blanks (MB): Prepare a minimum of one MB per batch of samples prepared or one per twenty samples, whichever is more frequent.

7.2 Laboratory Control Standards (LCS). Prepare a minimum of one set of duplicate LCS per batch of samples prepared or one set per twenty samples, whichever is more frequent.

7.3 Calibration Verification Standards (CCV, CCB). Run a CCV and CCB at the completion of every ten samples.

8.0 PREPARATION RATE

Set-up and preparation of standards requires two hours. Samples are prepared at the rate of twenty-five per hour. Autoclave at the rate of twenty-five samples per two hours.

9.0 SAFETY

Fully fastened labcoat and safety glasses must be worn. Nitrile gloves must be worn when handling nitric or sulfuric acid. All chemical containers should be clean and properly labeled. Immediately cleanup any materials spilled on the floor, in hoods or on bench tops. All damaged or broken glass should be discarded immediately. The autoclave must be depressurized slowly to prevent samples from boiling over.

Date: 09/08/89
Revision No.: 2
Revised by: GLR
Approved by:

1. TITLE: Heat of Combustion by Bomb Colorimeter (BTU)
Ref: ASTM D240
SOP #15-009

Container, preservation, and holding times may vary and is dependent on sample matrix, method of choice, regulatory compliance, and/or specific contract or client requests. Listed below are the holding times and the references that include container and preservation requirements for compliance with the safe Drinking Water Act (SDWA) and The Clean Water Act (CWA).

<u>REGULATION</u>	<u>HOLDING TIME</u>	<u>REFERENCE</u>
CWA	28 Days	CFR 40 pt. 136.3
SDWA	28 Days	EPA-570/9-82-002

2. SUMMARY:

Heat of combustion is determined by burning a specific amount of a sample in an oxygen bomb colorimeter. Without losing any of the sample or its combustion products, the burning process converts any solid or liquid combustible sample into soluble form ready for analysis. All hydrocarbons are oxidized to carbon dioxide and water during the reaction, while sulfur compounds are converted into oxides and absorbed in a small volume of water in the bottom of the bomb. Any mineral constituents remain as ash while other inorganic elements such as arsenic, boron and any halogens are recovered in the bomb washings. The heat of combustion is computed from the change of temperature before and after ignition, with proper allowances or thermochemical and heat transfer corrections.

INTERFERENCES:

None

DETECTION LIMIT:

500 BTU/lb

3. INSTRUMENTATION and EQUIPMENT/APPARATUS:

Parr Adiabatic Colorimeter
Parr 1901 Oxygen Bomb apparatus
Analytical balance
Oxygen tank
Sample bomb cups

4. PREVENTATIVE MAINTENANCE:

- 4.1 Check the seal on the oxygen bomb periodically for cracks and wear. Replace if necessary to prevent oxygen leakage.
- 4.2 The water bath before ignition should range from 22 C to 27 C to prevent the temperature from going out of range on the thermometer.
- 4.3 The analytical balance should be leveled and zeroed before weighing samples.
- 4.4 Sample cups should be soaked in nitric acid, scrubbed and dried at 105 C before using.

5. REAGENTS:

- 5.1 Methyl Red Indicator: Dissolve 100 mg methyl red in 100 ml ethyl alcohol.

Life of Reagent: one year
Storage Requirements: none

- 5.2 0.0725N NaOH Solution: In a 1000 ml volumetric, dissolve 2.9 g NaOH in 800 ml DI water. Place in water bath on a stir plate. Mix well. Bring to volume with DI water.

Life of Reagent: one year
Storage Requirements: none

- 5.3 Ethylene glycol - purchased from CMS

- 5.4 Benzoic acid - purchased from CMS

6. PROCEDURE:

6.1 SAMPLE SIZE:

Approximately 1 gram of sample is used. If ethylene glycol or benzoic acid is used, approximately 0.5 grams of sample is used with approximately 0.5 grams of ethylene glycol or benzoic acid. (Ethylene glycol is added to a solid sample which will not burn by itself. Benzoic acid is added to a liquid sample which does not burn.

6.2 Standardization:

A benzoic acid tablet (0.9 g - 1.25 g) is analyzed twice. The average value obtained from these two runs is a constant, W. The W value is re-analyzed after every 10 samples, not to exceed 13 for each bomb in the following procedure.

6.3 Analytical Sequence:

<u>Quality Controls</u>	<u>Frequency</u>	<u>Control Limit</u>
Preparation Blank (PB)	1 in 20 samples	control chart
Lab Control Stand. (LCS)	1 in 20 samples	control chart
Lab Control Stand. Dup.	1 in 20 samples	control chart
Matrix Duplicate	1 in 20 samples	control chart

6.4 Preparation of Quality Controls:

6.4.1. Preparation Blank (PB) - bomb one benzoic acid tablet of about 1.0 g and use washings for procedural check in % Sulfur analysis.

6.4.2. Lab Control Standard (LCS) and LCS Duplicate - Bomb one benzoic acid tablet of about one gram.

6.5 Procedure:

6.5.1. Weigh out approximately 1.0 g of sample (making the necessary allowances when ethylene glycol or benzoic acid is used) on an analytical balance.

6.5.2. Add a small amount of DI water to the bomb, and seal the bomb shut.

6.5.3. Purge the bomb with oxygen to 30 atmospheres. DO NOT OVERCHARGE THE BOMB! If by accident the oxygen introduced into the bomb should exceed 40 atmospheres, do not proceed to combustion. An explosion could occur with possible violent rupture to the bomb. Release the air pressure and proceed in the usual manner.

6.5.4. Use the same amount (0.5 g) of DI water in the colorimeter vessel for each test. To do so, empty the entire water reservoir into the colorimeter for each analysis.

6.5.5. Assemble the colorimeter in the jacket, making sure the stirrer is revolving.

6.5.6. Allow the temperature to equilibrate, and record the initial temperature.

6.5.7. When both thermometers are the same (0.01), push the igniter button and watch for the temperature to rise.

6.5.8. After six minutes of from firing, begin reading the temperature every minute.

6.5.9. When the temperature is the same for three

consecutive minutes, record the final temperature. (If the temperature does not rise, sample will have to be re-analyzed.)

- 6.5.10. Remove the bomb and release the pressure at a uniform rate in a fume hood.
- 6.5.11. Examine the interior of the bomb to confirm that combustion was complete (small amounts of ash may be present).
- 6.5.12. Measure the unburned firing wire, subtract from the original length and record as residual wire (calories).
- 6.5.13. Wash the interior of the bomb with DI water.
- 6.5.14. Collect the washings into a graduated cylinder.
- 6.5.15. Bring up to a volume of 250 ml or 500 ml, depending on the number of analysis to be performed on the sample.
- 6.5.16. Titrate 50 ml of the washings with 0.0725N NaOH, using methyl red indicator.

7. CALCULATIONS:

7.1 Standard Value of Bomb (W):

$$W = \frac{Hm + e}{t}$$

Where: e = residual wire in calories
H = heat of combustion of benzoic acid in cal/gram
m = mass of benzoic acid used
t = temperature rise

7.2 BTU/lb:

$$\text{BTU/lb} = \frac{[t(W) - \text{NaOH}(d) - \text{E.G. or B.A.} - \text{Res.wire} - X]}{\text{Sample Weight (g)}}$$

Where: t = change in temperature,
W = Standard Bomb Value,
NaOH = mls 0.0725 N NaOH titrated,
d = dilution factor (if final volume is 250 ml, then d = 5; if final volume is 500 ml, then d = 10),
E.G. (ethylene glycol) = (4425 cal/g) (gms E.G.)
B.A. (benzoic acid) = (6318 cal/g) (gms of B.A.)

Res.wire = amount of burned wire in calories
X = % Sulfur, if % Sulfur is >0.1% then:
X = (%S) (14) (sample wt. in gm)

7.3 LCS and LCS Dup % Recovery (%R):

$$\%R = \frac{\text{observed concentration}}{\text{actual concentration}} \times 100$$

7.4 Matrix Dup. and LCSD Relative Percent Difference (RPD):

$$RPD = \frac{\text{difference}}{\text{mean}} \times 100$$

8. QUALITY CONTROL:

At least one method blank and at least two Lab Control Standards (LCS) will be included in each laboratory lot of 20 samples. Regardless of the matrix being processed, the LCS and method blanks will be in an aqueous media.

The method blanks will be examined to determine if contamination is being introduced in the laboratory.

The LCS will be examined to determine both precision and accuracy.

Accuracy will be measured by the percent recovery (%R) of the LCS. The recovery must be in range, as determined by statistical analysis, in order to be considered acceptable. Additionally, %R will be plotted on control charts to monitor method accuracy.

Precision will be measured by the reproducibility of both LCSs and will be calculated as Relative Percent Difference (RPD). Results must agree within statistical control limits in order to be considered acceptable.

9. CORRECTIVE ACTIONS:

9.1 Listed below are steps to be taken when an out of control situation occurs. The analyst MUST:

- 9.1.1. demonstrate that all of the problems creating the out of control situation were addressed,
- 9.1.2. document the problem and the action that was taken to correct the problem on a corrective action report form,
- 9.1.3. document on a corrective action report that an in control situation has been achieved, and
- 9.1.4. receive approval (signature) of the unit leader, QA personnel, or the laboratory manager prior to the release of any analytical data associated with the problem.

9.2 Listed below are some suggested courses of actions that may be taken to correct out of control situations that may occur with this procedure:

9.2.1. Laboratory Control Standards (LCS):

- If the LCS is low;
- determine the source of error within the sample preparation and repeat the set, WRITE A CAR.
- If the LCS is high;
- check for source of contamination,
- correct for contamination and repeat set, WRITE A CAR.

9.2.2. Laboratory Control Standard Duplicate (LCSD):

- The LCS duplicate must meet all control limits as LCS in addition to limits set for precision (same corrective action as LCS).

9.2.3. Preparation Blank (PB):

- reanalyze PB to verify that it is beyond detection limit;
- check and correct for any source of contamination,
- repeat sample set,
- in the extreme case where all samples in the set are at least ten times greater than the PB, reanalysis will not be required, WRITE A CAR.

9.2.4. Matrix Duplicate:

- the sample must be reprocessed and reanalyzed;
- if the reanalysis is still out of control, then the sample set will be ticked with a "N";
- regardless of the outcome of the reanalysis, a CAR will be written and approved.

10. HEALTH and SAFETY:

As always, general laboratory safety practices should always be followed. Waste samples should be handled with care due to the uncertainty of the properties and contents involved. Refer to the specific MSDS for the hazardous properties of any chemical or reagent involved in this procedure.

Many samples for BTU are hazardous. Therefore extra caution should be used when handling the samples. Wear safety glasses, gloves and a lab coat if desired.

Release the oxygen from the bomb under a fume hood.

21-15-0245.6

[illegible]

HEAT OF COMBUSTION BY BOMB CALORIMETER (BTU)

**ASTM D240
WESTON SOP 15-009**

METALS: MERCURY (SP NO. 21-15-0245.1)

- Mercury Digestion
- Mercury

Amendments to SOP of Method 0245.1 (SOP #21-15-0245.1)

1. Both SOPs presented are applicable for the analysis of mercury in the soils/sediments at SADA. The second SOP presented (Revision 03) will be chosen first for use since the analytical equipment is newer. However, based on availability of the equipment, the first SOP (Revision 02) and corresponding analytical equipment may be utilized. If mercury analysis by Revision 02 of the SOP is performed, then sample digestion will be done by the SOP of Method 0245.6.
2. Matrix spike and duplicate samples will be analyzed at a frequency of 1 per 20 investigative samples or 1 per 7 days (whichever is more frequent) for this project.
3. For the SADA removal project, a standard EPA method calibration will be done as described in Subsection 13.5 of the SOP.



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OPERATING PRACTICE
MERCURY

Eff. Date: 06/22/91 Initiated By: Dianne S. Therry Approved By: Jack R. Tuschall Authorized By: Marty J. Vollandt SP No. 21-15-0245.1

**INORGANIC ANALYSIS PROTOCOLS
METALS: MERCURY**

These Approval Signatures Are Kept on File
with WESTON's Analytics Division
QA Standard Practice Records

REVISION NUMBER: 03

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INORGANIC PREPARATION AND ANALYSIS PROTOCOLS
METALS: MERCURY

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REVISION NUMBER: 03

1.0 PURPOSE

Determination of mercury in aqueous and nonaqueous media.

2.0 REFERENCE

EPA-600/4-79-020, Methods for Chemical Analysis of Water and Wastes, Method 245.1

U.S. EPA CLP Inorganic Analysis, Multi-Media, Multi-Concentration SOW 788, Revised 2/89

3.0 PRINCIPLE

The flameless AA procedure is a physical method based on the absorption of radiation at 253.7 nm by mercury vapor. The mercury is reduced to the elemental state and swept from solution and passed through a cell of a double beam AA. Absorbance is a function of mercury concentration.

4.0 INTERFERENCES

Chloride, sulfide, certain volatile organic materials.

5.0 OPTIMUM CONCENTRATION RANGE

0.2 ug/L - 10 ug/L
0.1 ug/L - 10.0 ug/L (Pease AFB)



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6.0 INSTRUMENT DETECTION LIMIT

Approximately 0.02 ug/L.

7.0 REAGENTS

7.1 Sodium chloride-hydroxylamine sulfate solution: prepare by dissolving 12 g of sodium chloride and 12 g of hydroxylamine sulfate in sufficient deionized water to make 100 mL of solution.

7.2 Stannous chloride solution: prepare by dissolving 10 g of stannous chloride in 10% hydrochloric acid to make 100 mL of solution.

7.3 Di Water Type II

7.4 Potassium Permanganate, 5% (W/V)

7.5 Potassium Persulfate, 5% (W/V) (aqueous only)

7.6 Hydrochloric Acid, Conc. (soil only)

7.7 Nitric Acid, Conc.

7.8 Sulfuric Acid, Conc. (aqueous only)

8.0 STANDARDS

Refer to WESTON Mercury Preparation Operating Practice 21-15-0245.6.

9.0 INSTRUMENT PARAMETERS

Instrument: Leeman Labs Model PS200 Automated Mercury Analyzer

10.0 PRESERVATION

Acidify to pH <2 at the time of collection.

11.0 HOLDING TIME

28 days from collection, 14 days for drinking water samples.



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12.0 PREPARATION

12.1 See Tables 1 and 1A

12.2 See Table 2 for Water Analyses

13.0 PROCEDURE

13.1 Routine Operation

13.2 Preparing the System

The following procedures must be performed each morning before warming up the system:

- Pres the F10 macro key to stop any currently running macro.
- Change the drying tube. Refer to the Maintenance section 14.0 for instructions.
- Release the clamps and check the pump tubing for wear. Under normal use, the tubes will need to be replaced once a week. To replace tubing, refer to the Maintenance section 14.0 for instructions.
- Check the reductant volume and refresh, if needed.
- Clean the rinse tank using standard lab cleaning practices, add fresh rinse.
- If the lamp has been off then turn on the lamp power and allow the lamp to warm up for at least 45 minutes.
- If system is shut off, power up all components and perform COLDSTRT macro.

You are now ready to start up the system.

12.3 Startup Procedures

The startup routine you will use depends on the current state of the system. If it is in Overnite mode, use the



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Warmstart macro (Section 12.3.1). If the system has been completely powered down, you will need to run the Coldstart macro instead (Section 12.3.2).

12.3.1 Warm Start

The Warmstart macro is used to prepare the PS200 for operation if it is being started up from a short-term (overnight) shutdown.

To run the Warmstart macro, press the F2 macro key on the keyboard. Type WARMSTRT and press ENTER. The system will wait for several minutes and then turn on the pump and the gas flow to protocol speed. When the system is stable, a beep will sound and an "Operation complete" message will appear on the screen. The PS200 is now ready for operation.

12.3.2 Cold Start

The Coldstart macro procedure is used to prepare the PS200 for operation if the system has been shut down for an extended period of time. This procedure turns on the liquid and the gas flow and then waits until the system thermally equilibrates before beeping to indicate that it is ready to run. You should then perform an aperture test and make any necessary adjustments to the aperture before you run samples.

To run the Coldstart macro, press the F2 macro key on the keyboard, type COLDSTRT and press ENTER. The Coldstart procedure takes approximately 2 1/2 hours. Do not attempt to operate the PS200 before this procedure is complete, or its performance will be significantly impaired.

When a beep has sounded and an "Operation complete" message is visible on the screen, indicating the completion of the Coldstart procedure, you must check the apertures on the optical cell and make any necessary adjustments; this procedure is documented in Section 2.10, steps 1 and 2 of the operator's manual. When the aperture adjustments are completed, the PS200 is ready for operation.



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13.4 Software Setup

In order to run samples, you must enter all necessary information regarding the protocol, sample ID's, calibration values, and autosampler parameters into the software. This information is entered into a series of screens which are accessed from the Main Menu (Figure 13-1). (You can display the Main Menu at any time by pressing the F1 key on your keyboard.)

Perform each of the following steps in sequence to set up the software. When you have completed these steps, the PS200 will be able to run samples automatically.

NOTE: The steps below comprise the basic daily software setup sequence. The PS200 software also contains numerous advanced functions. Refer to the PS Series Reference Guide for a detailed description of the many other keys and functions available for use with this system.

Name the Protocol: Protocols are operational determinations (parameters) for running calibrations and samples. You must name the desired protocol to instruct the PS200 what its normal operational values will be for running the next batch of samples.

1. From the Main Menu, select PROTOCOL and then select Get. The Protocol screen will appear a "Get protocol name:" message will be displayed at the bottom of the screen (Figure 13-2).
2. Type the protocol name and press -ENTER. This creates a protocol file.
3. Press the F1 key to return to the Main Menu.

Name the Folder:

Once you have named the protocol, you must create a folder to hold all data generated from each sequence of operation.



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1. From the Main Menu, select DATA OUTPUT and then select Open folder. The Folder maintenance screen appears and an "Enter folder name:" message will be displayed at the bottom of the screen (Figure 13-3).
2. Type a folder name and press ENTER. The folder is created.
3. - Press the F1 key to return to the Main Menu.

Verify Values and Integration Times

You must now check to make sure that all values and integration times are correct for running the samples:

1. From the Main Menu, select PROTOCOL, then select Set Values. The Set Values screen (Figure 13-4) appears.
2. For normal operation, enter the following values (as illustrated above):

Number of integrations:	1
uptake time	10
Weight	N
Dilution	N
Percent Recovery	N
3. Press F1 to return to the Main Menu.

Enter values for on/off, times, and gains

1. From the Main Menu, select PROTOCOL, then select On/off, times, gains. The On/off, times, gains screen (Figure 13-5) appears and an "Enter integration time:" message is displayed at the bottom of the screen.
2. Type the desired integration time from between 1 and 30 seconds (the typically selected value is 10 seconds) and press ENTER.
3. Press the F1 key to return to the Main Menu.



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Enter the Calibration Standard Concentrations:

1. From the Main Menu, in sequence, select CALIBRATION, Standards, and then Units. The Units screen (Figure 13-6) appears and an "Enter units:" prompt is displayed at the bottom of the screen.
2. Type the desired unit of measurement (e.g., ppb) and press ENTER. Your entry will appear in the Units column above.
3. Using the hot key, select each standard on the screen (S1-S6) and enter the appropriate calibration standard concentration (e.g., S1-.00000, S2-.50000, S3-1.0000, S4-2.0000, S5-5.0000).

NOTE: Do not be concerned with the UI (Update Intercept) and US (Update Slope) columns at this time. If you want more information of these fields, refer to your PS Series Reference Guide.

4. Press the F1 key to return to the Main Menu.

Reset the Calibration Intensity Data:

1. From the Main Menu, select CALIBRATION, Reset, and New calibration reset. The Reset screen (Figure 13-7) appears at the bottom of the screen.
2. To erase any calibration data that may have already been done with this protocol, enter Y and press ENTER. An "All Data Reset" message will appear when the process is complete. (To escape this procedure, enter N instead.)
3. Press the F1 key to return to the Main Menu.

Set the Autosampler Rinse Time:

1. From the Main Menu, select AUTOSAMPLER, Setup, and Rinse time (seconds). The Setup screen (Figure 13-8) appears and an "Enter rinse time:" message is displayed at the bottom of the screen.
2. Type the desired value in seconds (typically 50) and press ENTER.



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3. Press the F1 key to return to the Main Menu.

Set up the Racks:

1. From the Main Menu, select AUTOSAMPLER and then Rack entry. The Rack screen (Figure 13-9) appears and an "Enter rack name:" message is displayed at the bottom of the screen.
2. Type a rack name (either new or existing) and press ENTER. (If you enter a new name, you will be asked if you want to create a new rack: answer Y.)
3. Fill the sample cups to be used to within 1/4" from the top (to allow for two runs). Using the Autosampler layout in Figure 13-10 as a guide, load each sample cup into the rack and enter the sample ID into the appropriate (cup) position on the Rack entry screen. Figure 13-11 contains an example of a completed rack entry screen.

NOTE: For details on the INSERT key, rack calculation options, and advanced editing options, refer to the PS Series Reference Guide.

4. It is important to remember that the PS200 can run two complete racks unattended.
5. Press the F1 key to return to the Main Menu.

Define start-to finish sample sequence:

1. From the Main Menu, select AUTOSAMPLER and then Setup. Type the rack number to be run (1 or 2). The prompt "Enter rack name" is displayed at the bottom of the screen.
2. Type the rack name and press ENTER. The Setup screen for that rack will appear and a "Begin cup:" prompt will be displayed at the bottom of the screen.
3. Enter the number (cup position; see Figure 13-10) of the first cup to be sampled and press ENTER. An "End cup:" prompt will now be displayed at the bottom of the screen.



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4. Enter the number of the last cup to be sampled and press ENTER. Figure 13-12 shows a sample Setup screen with a "from cup" entry of 1 and a "to cup" entry of 44.
5. Press the F1 key to return to the Main Menu.
6. If you are using a second rack, repeat steps 1-5.

13.5 Calibrating the System

The PS200 must be calibrated before you can run samples:

To perform a standard EPA (method 7470) calibration. Press the F2 macro key and "Macro:" prompt appears at the top of the screen (Figure 13-13) Type AUTOCLP and press ENTER. The calibration routine will begin running. It is assumed that the five standards (0, 0.5, 1.0, 2.0, 5.0, and 10.0 ppb) have been loaded as standards 1 through 5. After the standards run, the check standards will run automatically. AUTOCLP will accept the calibration. "Macro:" RUNSTD will run standards only.

To perform a calibration other than a standard EPA procedure, press the STD F6 action key. The Standard screen appears and a "Run standard: 1 2 3 4 5 6" message is displayed at the bottom of the screen. Enter the number of the standard to be run (1-6) and press ENTER. A "from replicate: 1 to: " message will then be displayed at the bottom of the screen. Enter the first number in the "from replicate:" field and last number in the "to:" field. Press ENTER. The system will run the standards.

NOTE: To stop a procedure at any time, press the Stop F10 action key.

The results of the calibration are automatically stored. To review the results, select CALIBRATION from the Main



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Menu and then select Line calibration to generate a display (see Figure 13-14 for example). Below are some guidelines for determining whether the results are acceptable:

- Do the %RSD's look acceptable for various concentrations?
- Is the correlation coefficient larger than .995?

If the calibration results are acceptable, type A and press ENTER. A "New calibration coefficients stored" message will be displayed at the bottom of the screen and you can begin running samples.

If the calibration results are unacceptable, rerun the standards to verify them or look at the Troubleshooting guide for further assistance. When you have achieved acceptable results, type A while in the Line Calibration page. A "New calibration coefficients stored" message will be displayed at the bottom of the screen and you can begin running samples.

13.6 Check Standards

This option allows you to verify that the calibration has not drifted. To check standard concentrations:

1. From the Main Menu, select CALIBRATION and then select check standards. The Check Standard screen will appear (Figure 13-14).
2. Type 1 for a check standard blank. Enter, in units specified on the standards page, the range of acceptance.
3. Type 2 for check standards cup 2. Type the concentration and Enter. Type the percent acceptance and Enter.
4. Repeat this for up to seven check standards.

From Main Menu, select AUTOSAMPLER, then select Setup and then check. Enter the C1 frequency (e.g., 5/EPA protocol)



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Halt: Enter Y if the instrument should halt after an unacceptable check standard. Enter N for an alert only. Macros can be written to automatically reanalyze and rerun samples if check standards fall outside specifications.

13.7 Running Samples

1. Press the F8 macro key. The Autosampler setup menu appears and a "Press F8 again to run sample" message will be displayed at the bottom of the screen.
2. Press the F8 macro key again. The PS200 will run the samples, print the results, and store the data in the folder you created.

NOTE: Each sample takes approximately 2 minutes to run; a full tray (88 samples) will take approximately 2 1/2 hours to complete. As operation is fully automatic, laboratory personnel need not be present while samples are running.

3. When all samples have been run, the system will beep and the word "Idle" will appear in the State field at the top of the screen. At this time, you can repeat steps detailed Sections 13.1-13.6 to run more samples, or you can shut down the instrument. Refer to Section 13.8 for shutdown procedures.

13.8 Shutdown Procedures

There are two methods for shutting down the PS200. Under routine operation, when the system is used daily, only the lamp is shut off (system power remains on) and the Overnight routine is used to put the unit into a "sleep mode". If the system is to be completely turned off and not used for an extended period of time, or if it is to



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be shipped or moved, you must use the long-term Shutdown routine instead. These two methods are described below. For weekends or periods of "sleep" greater than 24 hours it is recommended to turn off the mercury lamp using the blue button.

NOTE: Before shutting down the instrument, the system must have beeped to indicate completion of the last procedure, and the word "Idle" should appear in the "State" field in the top left of the displayed screen.

13.8.1 Short-Term (Overnite Macro)

Press the F2 macro key, type OVERNITE, and press ENTER. Turn off power to the lamp if the instrument will not be used for longer than 24 hours. In overnite mode, the pump and gas flow will turn on every few minutes, run for a few seconds, and then stop. This cycle exercises the tubes so they don't get flat spots and fatigue, and the gas flow keeps the optical cell dry.

SUGGESTION: If you will be automating your run procedures with macros, call the Overnite procedure at the end (CM....) so that the system will shut down automatically when the last procedure is finished.

13.8.2 Long-Term (Shutdown Macro)

The Shutdown macro procedure is designed to flush out all lines with DI water to get rid of any chemical residues.

1. Lift the sample tip and remove the rinse tray. Rinse and fill it with DI water and replace the tray. Lower the sample tip into the cleaned tray.
2. Remove the reductant bottle cap and line and carefully place the tip of the line in the rinse tank (rest the cap on the corner of the rinse tray).
3. Turn off the lamp.



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4. Press the F2 macro button. Type SHUTDOWN and press ENTER. When you hear a beep and the word "Idle" appears in the State field at the top left of the screen (you will have to wait several minutes), release all pump clamps.
 5. Remove the front cover of the PS200 and remove the optical cell (refer to Section 14.0). Disconnect the two gas lines on the left side of the cell and leave them hanging. Replace the optical cell and the front cover.
- NOTE: The next time you start up the system, you must remember to reopen the front cover, remove the optical cell and reconnect the gas lines.
6. Shut off power to the computer, monitor, printer, and finally the PS200.

14.0

MAINTENANCE

The PS200 requires some routine daily maintenance as well as some scheduled and non-scheduled periodic maintenance. All maintenance will be recorded in the instruments maintenance logbook. The following maintenance schedule lists the various maintenance procedures and when they should be performed. Each of these procedures is described in the following sections.

Maintenance Schedule

- | | |
|------------------------|---|
| • Drying Tube | Must be Changed Daily! |
| • Pump Tubing | Weekly, or as needed |
| • Lamp | Replace as needed (avg. 4 months-1 year) |
| • Optical Cell | Clean as needed (typically monthly) |
| • Liquid Gas Separator | Replace every 1-3 years, as needed |
| • Internal Tubing | Should not require replacement under normal circumstances |



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14.1 Packing and Changing the Drying Tube

Under normal use, the drying tube on the PS200 must be changed each morning before you run samples. (The drying tube is located on the front panel on the left side of the PS200) You may wish to pack several tubes at one time and store them in an airtight container so that you have a ready supply.

- **To pack a tube**, plug one end with quartz wool, pour in magnesium perchlorate to fill the tube, and plug the other end with quartz wool.

To change a tube, slightly loosen the nuts that hold the tube in at either end and slide the used tube out of the fittings. Slide a fresh tube into the fittings and tighten the fittings with your fingers to make a gastight seal.

To clean a tube, remove the quartz wool and the magnesium perchlorate. Either dispose of as a solid waste or dissolve in water and dispose of as a liquid waste. Clean the tube with ordinary laboratory glassware cleaner and dry thoroughly.

14.2 Replacing and Exercising Pump Tubing

Pump tubing should be replaced weekly or when it shows signs of wear.

There are four pump tubes: two for drainage, one for sample, and one for reductant. Each tube is fed through a pump cassette which then clamps onto the pump head. Slide a tube through the plastic clips at the bottom of a cassette until the plastic tab is secure. Hold the tube taut, slide the loaded cassette onto the pump head, and lock the clamp up. Repeat for the remaining tubes, then connect the tube ends.

For optimal performance, run DI water through new tubes for one hour to exercise them before using them for running samples. To do this, select INSTRUMENT from the Main Menu and then select Operation. The Instrument: Operation screen will appear. Set the Pump Rate flow to the standard rate of 5 mL/min (Type R and M and 5 Enter). Wait for one hour and then connect the tubing to the appropriate fluids. To turn the pump off type R and F.



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NOTE: This procedure only needs to be done once, when the tubes are new and unused.

14.3 Replacing the Lamp

The mercury lamp has a life of about 2000 hours, between four months and year of use. The lamp needs to be replaced if the relative absorbance of a standard has changed significantly while the optical cell is clean. If the lamp is suspected, it is faster to replace the lamp and recalibrate than to clean the optical cell.

NOTE: Before installation, clean the new lamp quartz with methanol and wipe it dry. Do not get finger prints on the lamp and do not face the printing on the lamp toward the optical cell.

To replace the lamp:

1. Turn off the lamp (press the blue button on the front of the PS200).
2. Remove the front panel of the PS200 (lift up and out).
3. Remove the optical assembly.
4. Remove the two screws on the lamp housing and take off the lamp cover.
5. Twist the lamp 90° and slide it straight out.
6. Insert the new lamp and rotate it 90° in the reverse direction to secure it in place. **Make sure that the lettering on the lamp will be facing to the left of the instrument when it has been reinstalled into the PS200. If it is not, remove the lamp and reinsert if correctly.**
7. Replace the optical assembly.

14.4 Cleaning the Optical Cell

If the relative absorbance of standards differs significantly from that of previous calibrations, the optical cell (located inside the front panel) may be dirty and must be cleaned:



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1. Turn the lamp and the PS200 power off and remove the front panel by lifting it up and out.
2. Remove the optics clamps, disconnect the detector, and rotate and lift out the assembly. Disconnect the gas lines.
3. Remove the six screws holding the lamp spacer and the detector spacer onto the optical cell.
4. - Inspect the two ends with the lenses. If the external surfaces of the lenses appear to be the only contaminant then clean. To clean use methanol. Install if no other cleaning is necessary.
5. Disassemble the optical cell (using the allen wrench provided on the inside of the front cover) by removing (in order) the screws, lens, and gasket at each end.
6. Carefully clean the inside of the cell with laboratory glassware cleaner, taking care not to scratch the inside surfaces. Rinse thoroughly, first with water and then with DI water. Dry the cell in the oven (free of contaminants) for one hour at approximately 40°-50°C.
7. Clean the lenses with laboratory glassware cleaner and rinse thoroughly with hot tap water. Flush lightly with methanol and dry by air or vacuum oven (maximum 50°C).
8. Replace the gaskets (this is recommended although not required unless the gasket shows signs of wear) and reassemble the optical cell. Cleaning of the gaskets should only be done with DI water.

14.5 Replacing the Liquid Gas Separator

The liquid gas separator (Transparent block on the chemical panel of the PS200) should only need to be replaced once every one to three years, depending on the amount of use it receives.

To replace the separator, shut off the gas and liquid flow and flush the tubing with DI water for safety



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purposes. Disconnect the four lines and remove the two screws. Remove the unit from the system, screw on a new one, reconnect the four lines, and turn the gas and liquid flow back on.

14.6 Replacing Internal Tubing

Internal gas and teflon tubes should last indefinitely and should not need to be replaced. Periodically inspect all tubing for restrictions or blockages. If tubing should need to be replaced, do so one piece at a time to avoid any confusion while making connections.

15.0 QUALITY CONTROL

Calibration curve must be composed of a minimum of a blank and five standards. Linear calibration curves must have a minimum correlation coefficient of 0.995, which must be reported with the raw data.

Calibration verification will be performed with a calibration blank and a continuing calibration verification (CCV) standard every ten samples and at the end of the analysis. The CCV must not vary more than 20% from its true value and must be prepared from a different source than the calibration curve standards.

Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve (dilute with a digested blank containing all reagents, or repeat the analysis using a smaller sample volume).

A minimum of one preparation blank must be analyzed per sample batch to determine if contamination has occurred. For this parameter, the continuing calibration blank (CCB) and preparation blank are equivalent.

Duplicate laboratory control samples (LCS) will be included with each sample batch of 20 samples. The analyzed result must not vary more than 20% from the true value. For this parameter, the LCS and CCV standard are equivalent.

Matrix spike and duplicate samples must be analyzed as requested by the client.



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16.0 CALCULATIONS

Perform a linear regression or quadratic fit analysis of the calibration standard results. Compare sample results to the curve to determine the mercury concentration.

FOR WATER:

$$\text{ug/L Hg} = \text{ug/L} \times \text{Dilution Factor}$$

FOR SOIL:

$$\text{mg/kg Hg} = \frac{(\text{ug/L}) \times \text{L} \times \text{Dilution Factor}}{\text{wt(g)} \times \text{fraction solids}}$$

17.0 METHOD PERFORMANCE

Laboratory control charts will be maintained for blanks and laboratory control standards. Accuracy and precision will be based on the laboratory control standards (i.e., although matrix spikes and sample duplicates are analyzed, they are not used for method control purposes).

18.0 ANALYSIS RATE

One analyst can set up and run a calibration curve in less than an hour. Sample analysis is conducted at an approximate rate of twenty to thirty per hour depending on mercury concentration.

19.0 SAFETY

Fully fastened lab coat, safety glassed and latex gloves must be worn.

All chemical containers should be clean and properly labeled.

Immediately cleanup any materials spilled on the floor, in hoods or on bench tops.

All damaged or broken glassware should be discarded immediately.



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TABLE 1

MERCURY SOILS MIDI-DIGESTION PROCEDURE		
METHOD 7471 - Section 7.1	Midi Scale	Full Scale
Sample Weight	0.1 grams	0.2 grams
Reaction Vessel	Screw Cap, 25 X 200 mm, 75 mL capacity	BOD, 300 mL
DI Water, Type II	2.5 mL	5 mL
Aqua Regia, 3:1 Hydrochloric Acid (conc) to Nitric Acid (conc)	2.5 mL	5 mL
Preparation	Water Bath, 2 hrs @ 95°C; Cool.	Water Bath, 2 hrs @ 95°C; Cool.
DI Water, Type II	25 mL	50 mL
Potassium Permanganate, 5% solution (w/v)	7.5 mL	15 mL
Preparation	Water Bath, 30 min @ 95°C; -- Cool.	Water Bath, 30 min @ 95°C; Cool. -
Hydroxylamine Addition	3 mL	6 mL
Total Volume	40.5 mL	81 mL
Proceed to stannous chloride addition and mercury analyses		



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TABLE 1A

MERCURY SOILS MIDI-DIGESTION PROCEDURE		
METHOD 7471 - Section 7.2 (Alternate Digestion Procedure)	Midi Scale	Full Scale
Sample Weight	0.1 grams	0.2 grams
Reaction Vessel	Screw Cap, 25 X 200 mm, 75 mL capacity	BOD, 300 mL
Sulfuric Acid (conc)	2.5 mL	5 mL
Nitric Acid (conc)	1 mL	2 mL
Potassium Permanganate (saturated)	2.5 mL	5 mL
Preparation	Autoclave, 15 min @ 121°C, 15 lbs	Autoclave, 15 min @ 121°C, 15 lbs
Dilute to Volume with Di water	50 mL	100 mL
Hydroxylamine Addition	3 mL	6 mL
Total Volume	59 mL	106 mL
Proceed to stannous chloride addition and mercury analyses		



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TABLE 2

MERCURY WATER MIDI-DIGESTION PROCEDURE		
METHOD 7471 - Section 7.1	Midi Scale	Full Scale
Sample Volume	33 mL	100 mL
Reaction Vessel	Screw Cap, 25 X 200 mm, 75 mL capacity	BOD, 300 mL
Sulfuric Acid (conc)	1.67 mL	5 mL
Nitric Acid (conc)	.83 mL	2.5 mL
Potassium Permanganate, 5% solution (w/v)	5 mL	15 mL
Potassium Persulfate 5% solution (w/v)	2.67 mL	8 mL
Preparation	Water Bath, 2 hrs @ 95°C. Cool.	Water Bath, 2 hrs @ 95°C. Cool.
Hydroxylamine Addition	2 mL	6 mL
Total Volume	45 mL	136.5 mL
Proceed with stannous chloride addition and mercury analysis		



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TABLE 3

mercstd.kdl

Working Calibration Standards for Mercury in Water

CALIBRATION STANDARDS			
STANDARD	mL OF STOCK	STOCK CONC. (ug/L)	FINAL VOLUME (mL)
blank	0.0	---	33.0
0.5 ug/L	0.165	100	33.0
1.0 ug/L	0.330	100	33.0
2.0 ug/L	0.660	100	33.0
5.0 ug/L	1.650	100	33.0
10.0 ug/L	3.300	100	33.0
ICV/CCV (5.0 ug/L)	0.165	1000	33.0

Working Calibration Standards for Mercury in Soil

CALIBRATION STANDARDS			
STANDARD	mL OF STOCK	STOCK CONC. (ug/L)	FINAL VOLUME (mL)
blank	0.0	---	50.0
0.5 ug/L	0.250	100	50.0
1.0 ug/L	0.500	100	50.0
2.0 ug/L	1.000	100	50.0
5.0 ug/L	2.500	100	50.0
10.0 ug/L	5.000	100	50.0
ICV/CCV (5.0 ug/L)	0.250	1000	50.0

Working calibration standards are made by pipetting the above volumes of stock standard and diluting to the above final volumes of digestate.



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TABLE 4
STANDARDS/SAMPLES PREPARATION

SAMPLES	STANDARDS
0.1 g	Blank - 10 mLs DI H ₂ O 0.5 - 9.75 mLs DI H ₂ O + stock std 1.0 - 9.5 mLs DI H ₂ O + stock std 2.0 - 9.0 mLs DI H ₂ O + stock std 5.0 - 7.5 mLs DI H ₂ O + stock std 10.0 - 5 mLs DI H ₂ O + stock std
2.5 mLs DI H ₂ O	volume of std. 10 mLs
2.5 mLs Aqua Regia	2.5 mLs Aqua Regia
H ₂ O bath 2 min. @ 95°C, cool	H ₂ O bath 2 min. @ 95°C, cool
Add 345 DI H ₂ O	Add 27 DI H ₂ O
7.5 mL KMnO ₄	7.5 mL KMnO ₄
water bath for 30 min. @ 95°C, cool	water bath for 30 min. @ 95°C, cool
3 mL Hydroxide	3 mL Hydroxide
final volume = 50 mL	final volume = 50 mL

* See Table 3 for working calibration standard concentrations

FIGURE 1
ANALYSIS RECORD

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SULFUR CONTENT

ASTM D129



Standard Test Method for SULFUR IN PETROLEUM PRODUCTS (GENERAL BOMB METHOD)¹

This standard is issued under the fixed designation D 129; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval. This is also a standard of the Institute of Petroleum issued under the fixed designation IP 61. The final number indicates the year of last revision.

This method was adopted as a joint ASTM-IP standard in 1964.

This method has been adopted for use by government agencies to replace Method 5202 of Federal Test Method Standard No. 791b.

¹ NOTE—Editorial changes were made throughout in July 1981.

Attention is called to Section 2.2 on Safety and to the specific precautionary directions incorporated in the method.

1. Scope

1.1 This test method covers the determination of sulfur in petroleum products, including lubricating oils containing additives, additive concentrates, and lubricating greases, that cannot be burned completely in a wick lamp. The method is applicable to any petroleum product sufficiently low in volatility that it can be weighed accurately in an open sample boat and containing at least 0.1 % sulfur.

NOTE 1—This method is not applicable to samples containing elements that give residues, other than barium sulfate, which are insoluble in dilute hydrochloric acid and would interfere in the precipitation step. These interfering elements include iron, aluminum, calcium, silicon, and lead which are sometimes present in greases, lube oil additives, or additive oils. Other acid insoluble materials that interfere are silica, molybdenum disulfide, asbestos, mica, etc. The method is not applicable to used oils containing wear metals, and lead or silicates from contamination. Samples that are excluded can be analyzed by ASTM Test Method D 1552, Test for Sulfur in Petroleum Products (High-Temperature Method).²

2. Summary of Method

2.1 The sample is oxidized by combustion in a bomb containing oxygen under pressure. The sulfur, as sulfate in the bomb washings, is determined gravimetrically as barium sulfate.

2.2 **Safety**—*Strict adherence to all of the pro-*

visions prescribed hereafter ensures against explosive rupture of the bomb, or a blow-out, provided the bomb is of proper design and construction and in good mechanical condition. It is desirable, however, that the bomb be enclosed in a shield of steel plate at least 13 mm thick, or equivalent protection be provided against unforeseeable contingencies.

3. Apparatus and Materials

3.1 **Bomb**,^{3,4} having a capacity of not less than 300 mL, so constructed that it will not leak during the test and that quantitative recovery of the liquids from the bomb may be achieved readily. The inner surface of the bomb may be made of stainless steel or any other material that will not be affected by the combustion process or products. Materials used in

¹ This test method is under the jurisdiction of ASTM Committee D-2 on Petroleum Products and Lubricants.

Current edition effective Aug. 31, 1964. Originally issued 1922. In 1949, revised incorporating former D 894. Replaces D 129 - 62.

In the IP, this method is under the jurisdiction of the Standardization Committee.

² *Annual Book of ASTM Standards*, Vol 05.01.

³ Criteria for judging the acceptability of new and used oxygen combustion bombs are described in ASTM Recommended Practice E 144, for Safe Use of Oxygen Combustion Bombs. *Annual Book of ASTM Standards*, Part 44.

⁴ A bomb conforming to the test specifications in IP Standard IP 12 is suitable.



the bomb assembly, such as the head gasket and lead-wire insulation, shall be resistant to heat and chemical action, and shall not undergo any reaction that will affect the sulfur content of the liquid in the bomb.

3.2 *Sample Cup*, platinum, 24 mm in outside diameter at the bottom, 27 mm in outside diameter at the top, 12 mm in height outside, and weighing 10 to 11 g.

3.3 *Firing Wire*, platinum, approximately No. 26 B & S gage, 27 SWG, or equivalent.

Caution—The switch in the ignition circuit shall be of a type which remains open, except when held in closed position by the operator.

3.4 *Ignition Circuit*, capable of supplying sufficient current to ignite the cotton wicking or nylon thread without melting the wire. The current shall be drawn from a step-down transformer or from a suitable battery.

3.5 *Cotton Wicking or Nylon Sewing Thread*, white.

4. Reagents and Materials

4.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.⁵ Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

4.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean distilled water or water of equal purity.

4.3 *Barium Chloride Solution (85 g/litre)*—Dissolve 100 g of barium chloride dihydrate ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$) in distilled water and dilute to 1 liter.

4.4 *Bromine Water (saturated)*.

4.5 *Hydrochloric Acid (sp gr 1.19)*—Concentrated hydrochloric acid (HCl).

4.6 *Oxygen*, free of combustible material and sulfur compounds, available at a pressure of 40 atm (41 kgf/cm²).

4.7 *Sodium Carbonate Solution (50 g/litre)*—Dissolve 135 g of sodium carbonate decahydrate ($\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$) or its equivalent weight in distilled water and dilute to 1 litre.

4.8 *White Oil, USP, or Liquid Paraffin, BP, or equivalent*.

5. Procedure

5.1 *Preparation of Bomb and Sample*—Cut a piece of firing wire 100 mm in length. Coil the middle section (about 20 mm) and attach the free ends to the terminals. Arrange the coil so that it will be above and to one side of the sample cup. Insert between two loops of the coil a wisp of cotton or nylon thread of such length that one end will extend into the sample cup. Place about 5 mL of Na_2CO_3 solution in the bomb (Note 2) and rotate the bomb in such a manner that the interior surface is moistened by the solution. Introduce into the sample cup the quantities of sample and white oil (Notes 3 and 4) specified in the following table, weighing the sample to the nearest 0.2 mg (when white oil is used, stir the mixture with a short length of quartz rod and allow the rod to remain in the sample cup during the combustion).

NOTE 2—After repeated use of the bomb for sulfur determinations, a film may be noticed on the inner surface. This dullness should be removed by periodic polishing of the bomb. A satisfactory method for doing this is to rotate the bomb in a lathe at about 300 rpm and polish the inside surface with emery polishing papers Grit No. 6, or equivalent paper,⁶ coated with a light machine oil to prevent cutting, and then with a paste of grit-free chromic oxide³ and water. This procedure will remove all but very deep pits and put a high polish on the surface. Before the bomb is used it should be washed with soap and water to remove oil or paste left from the polishing operation.

Caution—Do not use more than 1.0 g total of sample and white oil or other low sulfur combustible material or more than 0.8 g if the IP 12 bomb is used.

Sulfur Content percent	Weight of Sample, g	Weight of White Oil, g
5 or under	0.6 to 0.8	0.0
Over 5	0.3 to 0.4	0.3 to 0.4

NOTE 3—Use of sample weights containing over 20 mg of chlorine may cause corrosion of the bomb. To avoid this, it is recommended that for samples containing over 2 % chlorine, the sample weight be based on the chlorine content as given in the following table:

⁵ "Reagent Chemicals, American Chemical Society Specifications," Am. Chemical Soc., Washington, D.C. For suggestions on the testing of reagents not listed by the American Chemical Society, see "Reagent Chemicals and Standards," by Joseph Rosin, D. Van Nostrand Co., Inc., New York, N. Y., and the "United States Pharmacopeia."

⁶ Emery Polishing Paper Grit No. 6 may be purchased from the Behr-Manning Co., Troy, N. Y. Chromic oxide may be purchased from J. T. Baker & Co., Phillipsburg, N. J.

Chlorine Content percent	Weight of Sample, g	Weight of White Oil, g
2 to 5	0.4	0.4
Over 5 to 10	0.2	0.6
Over 10 to 20	0.1	0.7
Over 20 to 50	0.05	0.7

NOTE 4—If the sample is not readily miscible with white oil, some other low sulfur combustible diluent may be substituted. However, the combined weight of sample and nonvolatile diluent shall not exceed 1.0 g or more than 0.8 g if the IP 12 bomb is used.

5.2 *Addition of Oxygen*—Place the sample cup in position and arrange the cotton wisp or nylon thread so that the end dips into the sample. Assemble the bomb and tighten the cover securely. **Caution**—Do not add oxygen or ignite the sample if the bomb has been jarred, dropped, or tilted. Admit oxygen slowly (to avoid blowing the oil from the cup) until a pressure is reached as indicated in the following table:

Capacity of Bomb, ml	Minimum Gage Pressure, ^a atm kgf/cm ²	Maximum Gage Pressure, ^a atm kgf/cm ²
300 to 350	38 (39)	40 (41)
350 to 400	35 (36)	37 (38)
400 to 450	30 (31)	32 (33)
450 to 500	27 (28)	29 (30)

^a The minimum pressures are specified to provide sufficient oxygen for complete combustion and the maximum pressures represent a safety requirement.

5.3 *Combustion*—Immerse the bomb in a cold distilled-water bath. Connect the terminals to the open electrical circuit. Close the circuit to ignite the sample. **Caution**—Do not go near the bomb until at least 20 s after firing. Remove the bomb from the bath after immersion for at least 10 min. Release the pressure at a slow, uniform rate such that the operation requires not less than 1 min. Open the bomb and examine the contents. If traces of unburned oil or sooty deposits are found, discard the determination and thoroughly clean the bomb before again putting it in use (Note 2).

5.4 *Collection of Sulfur Solution*—Rinse the interior of the bomb, the oil cup, and the inner surface of the bomb cover with a fine jet of distilled water, and collect the washings in a 600-mL beaker having a mark to indicate 75 mL. Remove any precipitate in the bomb by means of a rubber policeman. Wash the base of the terminals until the washings are neutral to a suitable indicator. Add 10 mL of saturated bromine water to the washings in the beaker. (The volume of the washings is normally in

excess of 300 mL.) Place the sample cup in a 50-mL beaker. Add 5 mL of saturated bromine water, 2 mL of HCl, and enough distilled water just to cover the cup. Heat the contents of the beaker to just below its boiling point for 3 or 4 min and add to the beaker containing the bomb washings. Wash the sample cup and the 50-mL beaker thoroughly with distilled water. Remove any precipitate in the cup by means of a rubber policeman. Add the washings from the cup and the 50-mL beaker, and the precipitate, if any, to the bomb washings in the 600-mL beaker. Do not filter any of the washings, since filtering would remove any sulfur present as insoluble material.

5.5 *Determination of Sulfur*—Evaporate the combined washings to 200 mL on a hot plate or other source of heat. Adjust the heat to maintain slow boiling of the solution and add 10 mL of a BaCl₂ solution, either in a fine stream or dropwise. Stir the solution during the addition and for 2 min thereafter. Cover the beaker with a fluted watch glass and continue boiling slowly until the solution has evaporated to a volume approximately 75 mL as indicated by a mark on the beaker. Remove the beaker from the hot plate (or other source of heat) and allow it to cool for 1 hr before filtering. Filter the supernatant liquid through an ashless, quantitative filter paper (Note 5). Wash the precipitate with water, first by decantation and then on the filter, until free from chloride. Transfer the paper and precipitate to a weighed crucible and dry (Note 6) at a low heat until the moisture has evaporated. Char the paper completely without igniting it, and finally ignite at a bright red heat until the residue is white in color. After ignition is complete, allow the crucible to cool at room temperature, and weigh.

NOTE 5—A weighed porcelain filter crucible (Sela type) of 5 to 9-μm porosity may be used in place of the filter paper. In this case the precipitate is washed free of chloride and then dried to constant weight at 500 ± 25°C.

NOTE 6—A satisfactory means of drying, charring, and igniting the paper and precipitate is to place the crucible containing the wet filter paper in a cold electric muffle furnace and to turn on the current. Drying, charring, and ignition usually will occur at the desired rate.

5.6 *Blank*—Make a blank determination whenever new reagents, white oil, or other low-sulfur combustible material are used. When running a blank on white oil, use 0.3 to 0.4 g and follow the normal procedure.



6. Calculation

6.1 Calculate the sulfur content of the sample as follows:

$$\text{Sulfur, weight percent} = (P - B)13.73/W$$

where:

P = grams of BaSO_4 obtained from sample,
 B = grams of BaSO_4 obtained from blank,
 and
 W = grams of sample used.

7. Report

7.1 Report the results of the test to the nearest 0.01 %.

8. Precision

8.1 The precision of this test is not known to have been obtained in accordance with currently accepted guidelines (for example in Committee D-2 Research Report RR: D02-1007, "Manual on Determining Precision Data for ASTM Methods on Petroleum Products and Lubricants").

8.1.1 *Repeatability*—The difference between two test results, obtained by the same operator with the same apparatus under constant operating conditions on identical test material, would in the long run, in the normal and correct operation of the test method, exceed the following values only in one case in twenty:

8.1.2 *Reproducibility*—The difference be-

tween two single and independent results obtained by different operators working in different laboratories on identical test material would, in the long run, in the normal and correct operation of the test method, exceed the following values only in one case in twenty:

Sulfur, weight percent	Repeatability	Reproducibility
0.1 to 0.5	0.04	0.05
0.5 to 1.0	0.06	0.09
1.0 to 1.5	0.08	0.15
1.5 to 2.0	0.12	0.25
2.0 to 5.0	0.18	0.27

NOTE 7—The precision shown in the above table does not apply to samples containing over 2 % chlorine because an added restriction on the amount of sample which can be ignited is imposed.

NOTE 8—This method has been cooperatively tested only in the range of 0.1 to 5.0 % sulfur.

NOTE 9—The following information on the precision of this method has been developed by the Institute of Petroleum (London):

(a) Results of duplicate tests should not differ by more than the following amounts:

Repeatability	Reproducibility
$0.016x + 0.06$	$0.037x + 0.13$

where x is the mean of duplicate test results.

(b) These precision values were obtained in 1960 by statistical examination of interlaboratory test results.⁷ No limits have been established for additive concentrates.

⁷ IP Standards for Petroleum and Its Products, Part I, Appendix E.

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INORGANIC ANALYSIS PROTOCOL
% SOLIDS, % MOISTURE % ASH, AND % VOLATILE SOLID
DETERMINATION PROCEDURES

1.0 PURPOSE

- 1.1 To determine the percent moisture and solid composition of waste materials.
- 1.2 To determine the % ash or fixed solid and volatile solid composition of waste materials.

2.0 REFERENCES

- 2.1 Laboratory Determination of Water Content of Soil, Rock and Soil Aggregate Mixture, ASTM D2216-80. 04.08
- 2.2 Methods of Soil Analysis, Water Content Part 1, 21-2.2
- 2.3 Standard Methods for the Examination of Water, and Wastewater, 16th Edition, 1985. Method 209.0., Fixed and Volatile Solids Ignited at 550°C.

3.0 PRINCIPLE

- 3.1 Percent Solids and % moisture determinations are made by drying a moist material to a constant mass in a drying oven. The masses of the sample before and after the drying procedure are used in calculating the percent of moisture and solid content of the original sample.
- 3.2 Percent Ash and % Volatile Solids are determined by igniting an already dried sample in a 550°C oven. The mass that is left after ignition is the ash (or fixed solid) component, the mass that is lost is the volatile solid component.

4.0 INTERFERENCES

Non-representative particulates should be excluded from the sample if it is determined that their inclusion is not desired in the final result (i.e. large rocks).

5.0 METHOD DETECTION LIMIT

0.10%

6.0 OPTIMUM CONCENTRATION RANGE

0.10-100%

7.0 **REAGENTS**

None

8.0 **STANDARDS**

None

9.0 **INSTRUMENTAL PARAMETERS**

Any balance that can read 0.01 gram.

10.0 **PRESERVATION**

None

11.0 **HOLDING TIME**

None

12.0 **PROCEDURE**

12.1 Before starting, be sure that the balance has been checked with at least two Class P standard weights. These can be found in desiccator in the balance room. Document the weights in the balance log book found by each one of the balances. Ensure that the weights are at least $\pm 0.01g$ of their true value. If there is a problem, please contact your supervisor.

12.2 For % solids and % moisture determinations, weigh and record the weight of an empty aluminum pan to the nearest 0.01g. This is the tared weight.

12.3 Add 5-10g of sample to the tared aluminum pan. Weigh and record the weight to the nearest 0.01g.

12.4 Place sample and pan in drying oven set at 105°C. Dry the sample overnight (12-24 hours) but no longer than 24 hours. Note: Wear heat resistant gloves when handling hot containers. If the sample is dried less than 12 hours it must be documented that a constant weight was attained (see 12.5). If the drying time exceeds 12 hours proceed to section 12.6.

12.5 Constant weight determination:

12.5.1 Desiccate the sample for one hour, weigh and record to the nearest 0.01g. Place the sample back into the oven for at least one hour, desiccate re-weigh and record. Repeat process until constant weight is achieved.

- 12.5.2 Constant weight is achieved when the loss of weight is greater than 0.01g between each weighing.
- 12.6 Place the dried sample in a desiccator for at least one hour. Take the sample out of the desiccator and immediately weigh a record weight to the nearest 0.01g.

- 12.7 The calculation for % solids is as follows:

$$\% \text{ solids} = \frac{\text{Pan and dry sample wt.} - \text{pan wt.}}{\text{Pan and wet sample wt.} - \text{pan wt.}} \times 100$$

The calculation for % moisture is as follows:

$$\% \text{ Moisture} = 100\% - \% \text{ solids result}$$

- 12.8 Percent ash and % Volatile Solid determinations can be made using the dry sample obtained from the % solids or % moisture determination. Instead of using an aluminum pan a ceramic evaporating dish must be used.
- 12.8.1 Prepare the evaporating dish by drying it in a furnace at 550 ± 50°C for at least 20 minutes. Note: Wear heat resistant gloves when handling hot containers. Remove dish from furnace and let it cool partially in the air until most of the heat has been dissipated. Desiccate the dish for at least one hour, and proceed with % solids determination using the dish instead of the pans (12.2 to 12.7).
- 12.8.2 After the sample is dry, weigh and record the weight. Insert the dried sample in a furnace that is already warmed up to 550 ± 50°C. Ignite the sample for at least 20 minutes. Remove and desiccate as before (see 12.8.1). Weigh and record final weight of ashed sample.
- 12.8.3 Calculate % ash using this formula:
- $$\frac{\text{wt. of residue and dish after ignition} - \text{wt. of dish}}{\text{wt. of residue and dish before ignition} - \text{wt. of dish}} \times 100 = \% \text{ Ash}$$
- 12.8.4 Calculate % volatile solids using this formula.
- $$100\% - \% \text{ ash results} = \% \text{ Volatile Solids}$$
- 12.9 It is important to include the following information in the data book when doing % solids, % moisture, % volatile solid and % ash determinations:

- 12.9.1 Temperature and time in and out of the oven, or furnace.
- 12.9.2 Date analysis was started and completed.
- 12.9.3 ID of balance (the same balance must be used for all weighings)
- 12.9.4 Analysts signature for all entries.
- 13.0 QUALITY CONTROL
- 13.1 Analyze a minimum of one duplicate with every batch or every 2 samples.
- 13.2 Check the balance with at least 2 known standard weights each day.
- 15.0 METHOD PERFORMANCE
N/A
- 16.0 ANALYSES RATE
Samples can be weighed out at a rate of one every two minutes. The samples then have to be put in an oven for at least 12 hours, desiccated for one hour and weighed back at an approximate rate of one per minute.
- 17.0 SAFETY
Fully fastened lab coat, safety glasses and latex gloves must be worn.
Balances and ovens must be cleaned after use. Immediately clean up any materials spilled on floor, in hoods, or on bench tops.
All damaged or broken glassware should be discarded immediately

PERCENT MOISTURE, PERCENT ASH

**EPA METHOD 209F
(OP NO. 21-15-0160.6)**

METALS EMISSIONS IN EXHAUST GASES

EPA/530-SW-91-010

(SEE APPENDIX D - SAMPLING METHODS)

APPENDIX F**QUALITY ASSURANCE/QUALITY CONTROL (QA/QC) PLAN**
(Submitted as a separate document)